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Process Modeling and Techno-Economic Analysis of Micro-Encapsulated Carbon Sorbents (MECS) for CO₂ capture in a Fixed Bed and Moving Bed Reactors

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Process Modeling and Techno-Economic Analysis of Micro-Encapsulated Carbon Sorbents (MECS) for CO₂ capture in a Fixed Bed and Moving Bed Reactors

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to the Benjamin M. Statler College of Engineering and Mineral Resources at West Virginia
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in
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Abstract

Process Modeling and Techno-Economic Analysis of Micro-Encapsulated Carbon Sorbents (MECS) for CO₂ capture in a Fixed Bed and Moving Bed Reactors

Goutham Kotamreddy

Carbon capture, utilization, and storage (CCUS) is seen as a suite of technologies to curb the carbon dioxide emissions from the atmosphere and plays a crucial role to meet the net zero emissions target for many countries by 2050. One of the major sources for CO₂ emissions is combustion of fossil fuels to meet the electricity demands. The IEA report [1] projects the global electricity demands to rise by 80% over the next three decades. In the developing countries, coal will continue to play a dominant role in electricity production. Various innovative capture technologies are being explored because the state-of-the-art monoethanolamine (MEA) based carbon capture technology has drawbacks such as corrosion, energy penalty. There are several potential solvents that have lower energy penalty, but they are highly viscous or may turn into solid phase in the absorber or desorber thus making it difficult to use them in conventional towers. Micro-Encapsulated Carbon Sorbents (MECS) is a new, promising technology for the capture of carbon dioxide that could overcome some of the challenges associated with the highly viscous or phase change materials [2]. Microencapsulation is a microfluidic process where a substance is encapsulated within an inert polymer material. Microcapsules containing the solvent can be produced with diameters ranging from 100-600 microns. The small size of these microcapsules results in a high specific surface area per unit volume, which can enhance mass and heat transfer rates by orders of magnitude.

The aim of this research is to develop multiscale process models for MECS technology to better our understanding of operational and economical challenges. Using the rigorous multiscale modeling and simulation, the time, cost, and risks involved in the development of new carbon capture technologies can be significantly reduced [10]. Currently, the studies related to MECS in the literature are mainly focused on experimental demonstrations of technology on a lab scale [2,12]. However, the studies on operational and economic feasibility of MECS technology on a

pilot and industrial scale are lacking. Reliable mathematical models describing the complex mass and heat transfer in various types of potential contactors using MECS particles can help in identifying the challenges and advantages of MECS technology in an industrial scale. Both contactor technology and encapsulated solvent affect the performance of MECS system. Therefore, aim of this study is model-based investigation and optimization of contactor technologies, especially fixed bed and moving bed, and potential solvents so that commercialization potential of the MECS technology can be enhanced. In particular, equation oriented multi-scale mathematical models for both reactor configuration of MECS will be developed. The development of a capsule scale model considering the solvent characteristics is necessary to evaluate the performance of MECS in a reactor scale. The data from the experiments conducted at LLNL is used to obtain a maximum likelihood estimate of the initial solvent concentration inside the capsules and the parameters present in the capsule model. The reactor scale model includes a model of the capsule scale with sub-models of the physical and chemical properties, kinetics, mass, and heat transfer along with models of the bulk scale where mass and heat transfer and hydrodynamics are modeled. The multi-scale model considers both absorption and regeneration stages for a temperature swing system.

The goal of the research work is also to propose the optimal operating conditions for the explored reactor configurations. An economic based optimization using Equivalent annual operating cost (EAOC) of moving bed reactor is formulated in Aspen Custom Modeler. The solvent resides inside the microcapsules, and it is difficult to measure the concentration analytically. Hence, a soft sensing approach is proposed to estimate the solvent water content of the capsule. A control framework utilizing soft sensors is developed to minimize the water loss from the capsule and also maintain the key operating variables such as capture percentage and desorber bottom temperature at their desired levels. The sodium carbonate solution has been widely investigated experimentally by LLNL. Ionic liquids are another class of solvents that are water lean and shown to be promising for CO₂ absorption with their unique tunable characteristics. However, they suffer operational difficulties due to high viscosity and micro encapsulation of such solvents might prove to be an effective strategy [12]. In this study, two other potential solvents, specifically an ionic liquid and piperazine, are investigated. Further, the scope of the work also includes the techno-economic analysis of CO₂ absorption for a 644 MWe gross power plant to understand the commercial feasibility of this technology.

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NOMENCLATURE

A	Area [m^2]
a_e	Surface area to volume ratio [$1/\text{m}$]
C	Concentration of species [kmol/m^3]
C^*	Free species concentration in the liquid core [kmol/m^3]
C_p	Specific heat capacity [kJ/kgK]
d, D	Diameter [m]
D	Diffusivity of species [m^2/s]
ϵ_{bed}	Porosity of the bed
E	Enhancement factor
f_{H_2O}	Vapor pressure of water
H	Enthalpy [kJ/kmol]
h	Heat transfer coefficient [$\text{kW}/\text{m}^2\text{K}$]
$\bar{H}$	Partial molar enthalpy [kJ/kmol]
He_{CO_2}	Henry's constant of CO_2 [$\text{kPa m}^3/\text{kmol}$]
Ha	Hatta Number
k	Mass transfer coefficient [m/s]
K	Thermal conductivity [kW/mK]
K	Equilibrium constant
k_1	Rate constant for the kinetically controlling reaction
L	Length of the reactor [m]
N	Molar flux of the species [$\text{kmol}/\text{m}^2\text{s}$]
P	Pressure [kPa]
R	Radius [m]
T	Temperature [K]
u	Superficial velocity [m/s]
V_R	Volume of the reaction chamber [m^3]
μ	Viscosity [kmol/ms]
ρ	Density [kmol/m^3]
ϕ	Fugacity of the species
γ	Activity coefficient of the species
x	Mole fraction of species
EAOC	Equivalent annual operating cost
MEA	Monoethanolamine
TSIL	Task specific ionic liquid
PZ	Piperazine
MECS	Micro-encapsulated carbon sorbents
LMPC	Linear model predictive control
 <i>Subscript</i>	
c , core	Core part of the capsule
cap	Capsule
gs	Gas to solid interaction
g, G	Gas phase
hxw	Heat exchanger wall
$hxwG$	Heat exchanger wall to gas interaction
i	Species
int	Interface between liquid and shell
L	Liquid

s, shell

surf

sat

T

w

Shell part of the capsule

Surface of the capsule

Saturation

Total

Water

Chapter 1. Introduction

As per the Intergovernmental Panel on Climate Change (IPCC) Special Report [3] issued in 2019, anthropogenic activities are likely to have caused a global warming of approximately 1°C above pre-industrial levels. The goal of reducing the global temperature rise by 2°C set by Paris Agreement [4] requires a significant decrease in CO₂ emissions. Many strategies have been proposed to mitigate greenhouse gas emissions such as switching to less carbon-intensive fuels, using renewable energy sources, improving the efficiency of energy conversion devices, and CO₂ capture utilization, and storage (CCUS) [5]. The CO₂ emissions are expected to reach net zero by 2050 in many countries according to the IEA report [1]. The net zero emissions (NZE) can be achieved through various technological innovations and their deployments around the world. Carbon capture utilization and storage (CCUS) applications continue to play an important role in curbing emissions especially from the fossil fuel-based electricity production sector [6].

One of the major sources for CO₂ emissions is combustion of fossil fuels and the choice of combustion process directly impacts the CO₂ capture technology. Post-Combustion, Pre-Combustion, and Oxyfuel Combustion are the main three CO₂ capture systems rooted from the type of combustion process [7]. Of these capture technologies, post-combustion capture systems are very suitable for the existing power plants as they can be retrofitted reasonably easily. The CO₂ composition in the combustion flue gas is generally less, varying between 4-14%. In the post combustion capture technology, absorption of CO₂ using a liquid sorbent is currently the mature process. CO₂ from flue gas is absorbed into a liquid sorbent during absorption stage and the CO₂ is desorbed by heating in the regeneration stage. The major challenge for the post-combustion technologies is the significant parasitic load caused mainly due to the energy requirements in the regeneration stage for the removal of CO₂.

1.1. Micro-Encapsulated Carbon Sorbents (MECS)

Several advanced technologies are being developed for CO₂ capture because the state-of-the-art monoethanolamine (MEA) based carbon capture technology has several drawbacks such as corrosion, energy penalty [8,9]. There are several potential solvents that have lower energy penalty, but they are highly viscous or may turn into solid phase in the absorber or desorber thus making it difficult to use them in conventional towers. Micro-Encapsulated Carbon Sorbents

(MECS) is a new, promising technology for the capture of carbon dioxide that could overcome some of the challenges associated with the highly viscous or phase change materials [2]. Microencapsulation is a microfluidic process where a substance is encapsulated within an inert polymer material. The fabrication of microcapsules is done using double-capillary device where the fluids of interest are injected at different speeds, and this is referred as emulsification [2,11]. Microcapsules containing the solvent can be produced with diameters ranging from 100-600 microns. The small size of these microcapsules results in a high specific surface area per unit volume, which can enhance mass and heat transfer rates by orders of magnitude. Motivations behind encapsulation of a substance can widely vary. Immobilization of volatile material, release of a substance in a controlled manner over a period and managing phase separation are a few of the motivations. Microencapsulation can also be applied to process engineering applications that require handling of solids/slurry or highly viscous materials, bypassing operational issues such as clogging of equipment, high pumping cost, and lack of homogeneity in the process fluids.

Microencapsulated sorbents (solvents) comprise of two major components- polymer shell and encapsulated solvent. While encapsulating a solvent, compatibility between the polymer and the candidate solvent need to be evaluated. The pioneers of the MECS technology for CO₂ capture is Lawrence Livermore National Laboratory (LLNL), our collaborator in this research. LLNL has developed compatible polymers for several solvents for carbon capture. The well characterized microcapsule that has been experimentally studied and made available by LLNL for this work is sodium carbonate as the solvent and polymer shell made of polydimethylsiloxane (PDMS).

1.2. Multiscale Process Modeling

The herculean amount of research to reduce CO₂ emissions is resulting in several CO₂ capture technologies. The operational and economical hurdles involved in the demonstration of any new technologies at a commercial scale increases significantly as compare to a lab scale where they are shown to be promising. The process modeling studies comes to rescue in screening technologies at least to some extent by identifying the bottlenecks at different stages of technology readiness level [10]. Most of the chemical systems involve interactions on different characteristic length scales, molecular to reactor level interactions. Therefore, the confidence in such type of studies can be increased by implementing rigorous multiscale process models. The multiscale process

models aim to account for macroscale characteristics by incorporating microscale behavior in predicting the key performance indicators of the technology. In a nutshell, multiscale models are hierarchy of sub models that are interconnected to improve the accuracy of modeling predictions. The experimental demonstration of MECS technology has been done at lab scale so far [2,12,13] and its performance when scaled to address the industrial needs is studied very limited in the literature [14]. The experimental studies were also focused mainly on CO₂ absorption into the fabricated microcapsules and testing the compatibility of different solvents and polymers materials suitable to capsule formulation. The studies did not consider the water dynamics into and out of the capsule. The flue gas entering into the capture section from the power plant contains good amount of water content and it is important to consider its impact in the absorption stage. Also, the reaction of CO₂ with the encapsulated solvent is an exothermic reaction which will cause a temperature rise and that can lead to water drying out from the capsules if not operated properly. On the other hand, the desorption stage will be operated at higher temperatures to release CO₂ which again requires careful consideration to make sure that water does not bleed or transfuse from the capsules. The changes in the water content can result in capsule shape deformations and it is extremely difficult to account for the various shapes in a process modeling analysis. Few computational fluid dynamics (CFD) studies [15] can be seen in the literature which looked into swelling and buckling of capsules due to water dynamics. The multiscale modeling of MECS in a commercial level reactor configuration will enhance the understanding of possible improvements needed for it to be competitive to existing commercial capture technologies. This research tries to address the literature gaps in the MECS technology by developing multiscale process models that can be used to perform dynamic, optimization, and control related studies. The definite objectives of the research are summarized in the next section.

1.3. Objectives Summary

- To accomplish the modeling goals, this work uses AspenPlus, Aspen Custom Modeler (ACM), Aspen Process Economic Analyzer (APEA), Matlab/Simulink as the main platforms to develop multiscale models. The individual objectives are listed below,

- Develop a rigorous capsule model that interlinks the reaction, mass transfer, physio-chemical properties, and chemistry sub models to predict the system behavior at microscale level.
- Data reconciliation and parameter estimation to characterize the CO₂ mass transfer into microcapsule using the experimental data shared by LLNL.
- Develop a fixed bed model for MECS to simulate the absorption and regeneration stages of the CO₂ capture process.
- Develop a moving bed model for MECS to simulate the absorption and regeneration stages of the CO₂ capture process.
- Conduct techno-economic analysis on both fixed bed and moving bed CO₂ capture process for MECS technology.
- optimization
- Implement a soft sensing approach to estimate the encapsulated solvent concentration with the purpose to control and maintain a desired capsule water content.
- Develop a control framework using soft sensors to keep the key process variables like capture percentage, desorber bottom temperature, and capsule water content at desired set points.
- Compare the performance of MECS technology using different solvents, namely sodium carbonate, ionic liquids, and piperazine (PZ).

Chapter 2. Modeling of Microcapsule with Sodium Carbonate as Encapsulated Solvent

It is of crucial importance to have a detailed sub models that will only improve the macroscale predictions. The first experimental demonstration of microcapsule fabrication for CO₂ capture applications is carried out by LLNL group. Sodium carbonate is one of the encapsulated solvents considered for their experimental campaigns to study the applicability of microcapsules for CO₂ capture. In this chapter, a detailed capsule level model with Na₂CO₃ as encapsulated solvent is developed. The building components for the capsule model includes interaction with bulk gas phase, mass transfer through the polymer shell, kinetic model for the reaction of CO₂, and chemistry model that predicts the equilibrium behavior.

2.1. Introduction

The use of carbonate solutions to absorb CO₂, known as the Benfield process, has been widely studied [16-22]. Sodium carbonate is deemed to be a potential solvent for CO₂ capture due to variety of reasons, like the cost and eco-friendly nature, reaction with CO₂ is not only well characterized but also rate of reaction can be enhanced by using catalysts [17,19,20]. And the precipitation concerns at higher solvent weight percentages and CO₂ loadings can now be handled better with the encapsulation technique. Vericella et al. [2] at Lawrence Livermore National Laboratory (LLNL) first demonstrated microencapsulated carbonate solution for carbon capture. The same team at LLNL then showed carbon capture using ionic liquids [13]. More recently, the LLNL team demonstrated that a variety of capsules (including carbonates with and without catalysts) could absorb CO₂ effectively over 10 absorption/desorption cycles [12]. These studies have focused primarily on experimental demonstration of MECS. There are very few works on the mathematical modeling of MECS. A model of a single carbonate capsule has been developed to study the absorption reaction and water flux across the shell [15]. The authors here did not consider rigorous thermodynamics model that can capture the non-ideality of the electrolyte system and nonlinearity in the heat of absorption. The present work addresses these drawbacks by using rigorous eNRTL model to describe the thermodynamics of the solvent system. A simplified carbonate capsule model has been developed by LLNL and used an empirical model for the Na₂CO₃-CO₂-H₂O system to predict the CO₂ absorption rate in the presence of a catalyst [23].

This chapter focusses on the development of a rigorous capsule level model with a detailed thermodynamic model for the $\text{Na}_2\text{CO}_3\text{-CO}_2\text{-H}_2\text{O}$ system where simultaneous physical and chemistry equilibrium are considered. The chemistry model accounts for generation of the ionic species. These ionic species are taken into consideration in calculating excess Gibbs free energy which is used for computing activity coefficients in the electrolyte NRTL-based physical equilibrium approach. The enthalpy model is based on true species where excess enthalpy for Henry component (CO_2) is computed using Henry's constant while for remaining components, excess enthalpy is calculated based on activity coefficient. The heat of reaction of CO_2 with electrolyte systems can be nonlinear with respect to temperature and CO_2 loading. The thermodynamic model in this work capture variability in the heat of reaction as a function of temperature and CO_2 loading as opposed to a constant value used in most of the research work in this area. Developing an accurate kinetic model of this system and estimating model parameters is difficult. First, CO_2 diffuses through the shell membrane for absorption/desorption. Thus, any measured rate depends on the diffusion through the membrane and kinetics of reaction and simultaneous physical and chemical equilibrium in the bulk. Second, as the rate information is not directly measured by LLNL but rather the decreasing pressure in a batch system with time, estimation of parameters requires solution of a dynamic optimization problem. Third, as the solvent is encapsulated and its concentration can change over a period of time mainly due to transport of water through the membrane, there is a significant uncertainty in the solvent concentration.

The capsule model with the equations describing the diffusion through the shell and the reaction of CO_2 with encapsulated solvent is implemented in Aspen Custom Modeler (ACM)[®]. In order to complete the microcapsule model, the experimental data for sodium carbonate capsules shared by LLNL will be used to perform simultaneous data reconciliation and parameter estimation. This will be achieved by formulating an objective function based on maximum log likelihood to estimate the parameters that decreases the error between experimental and model data while subjected to constraints imposed by the capsule model. The mass transfer parameter of CO_2 through the shell and initial solvent concentration will be estimated in the capsule model. Finally, the results from the estimation will be used to compare the predictions from the capsule model and experimental data.

2.2. Experimental System

Figure 2.1 shows the schematic of the experimental setup used to study the CO₂ absorption using encapsulated carbonate solvent. The experimental data obtained from this setup is used to estimate parameters corresponding to the mass transfer model. The capsules are spread as a single layer on top of a mesh tray and placed in the reaction chamber. A pool of water is placed to achieve 100% humidity in the chamber. Before the start of the experiment, the ball valve is turned to vacuum pump to reach a minimum pressure value (~0.15 psi). Then, the vacuum pump is shutoff and the ball valve turned to CO₂ to release a fixed amount into the chamber. As the microcapsules start to absorb CO₂, the decrease in the gas pressure with respect to time is noted. More details about the experimental setup can be found in Vericella et al. [2]. The size of the microcapsules and the volume of the reaction chamber are provided in Table 2.1.

Figure 2.1. Experimental setup of CO₂ absorption using microcapsules filled with sodium carbonate.

Table 2.1. Size of the microcapsules and volume of the reaction chamber

Variable Name	Symbol	Value	Units
Capsule radius	R_{cap}	3e-4	m
Core radius	R_c	2.63e-4	m
Reaction chamber volume	V_R	4.5e-5	m ³

2.3. Capsule Model Development

This section of the chapter introduces the model of a single microcapsule along with the sub-models involved in its development.

2.3.1. Reaction, Thermodynamics, and Chemistry model. The overall reaction of CO₂ in the sodium carbonate solution is

The main reactions involved in the absorption of CO₂ using Na₂CO₃ solution are as follows [19,22]

The rate controlling step for this system is reaction (2.2). Reaction (2.3) is instantaneous. The chemistry can be described using the following reactions

As the sodium carbonate is a strong electrolyte, it is assumed to be completely dissociated in the water to form sodium and carbonate ions.

Equilibrium constants for the above reactions and the rate constants are obtained from the literature [17]. The eNRTL model in AspenPlus® is used to represent the thermodynamics of this system using model parameters from the literature [24]. Precipitation of solids upon reaction of CO₂ with carbonate solutions is observed for higher solvent concentrations and at high conversions of carbonate to bicarbonate. Precipitation of solids is not expected to occur for the solvent concentration and maximum solvent loading studied in this work [21,24]. Hence, the thermodynamic model does not account for any precipitation of solids.

The liquid molar enthalpy in the eNRTL model is calculated using solvent enthalpy, electrolyte enthalpy at infinite dilution, and excess molar enthalpy which is defined as

$$H_L = x_w h_w^o + \sum_k x_k h_k^{\infty,aq} + h^{*ex} \quad (2.8)$$

where w is water and k denotes electrolyte species. The solvent enthalpy is defined as

$$h_w^o = \Delta_f h_w^{ig} + \int_{298.15}^T c_{p,w}^{ig} dT + (h_w(T, P) - h_w^{ig}(T, P)) \quad (2.9)$$

The molar enthalpy of electrolyte species at infinite dilution is given as

$$h_k^{\infty,aq} = \Delta_f h_k^{\infty,aq} + \int_{298.15}^T c_{p,k}^{\infty,aq} dT \quad (2.10)$$

The molar excess enthalpy can be calculated using

$$h^{*ex} = -RT^2 \sum_i x_i \frac{\partial \ln \gamma_i}{\partial T} \quad (2.11)$$

where R is the gas constant. The elementary balance for all the species present in the Na_2CO_3 - CO_2 - H_2O system can be written as

$$C_{total \text{Na}_2\text{CO}_3,core} + C_{total \text{CO}_2,core} = C_{\text{CO}_2,core}^* + C_{\text{Na}_2\text{CO}_3,core}^* + C_{\text{HCO}_3^-,core} + C_{\text{CO}_3^{2-},core} \quad (2.12)$$

$$C_{total \text{H}_2\text{O},core} = C_{\text{H}_2\text{O},core}^* + C_{\text{HCO}_3^-,core} + C_{\text{OH}^-,core} + C_{\text{H}_3\text{O}^+,core} \quad (2.13)$$

$$C_{total \text{Na}_2\text{CO}_3,core} = C_{\text{Na}_2\text{CO}_3,core}^* + 0.5C_{\text{Na}^+,core} \quad (2.14)$$

$$C_{\text{Na}^+,core} + C_{\text{H}_3\text{O}^+,core} = 2C_{\text{CO}_3^{2-},core} + C_{\text{OH}^-,core} + C_{\text{HCO}_3^-,core} \quad (2.15)$$

The equilibrium relationship for the reactions (2.4-2.6) are given by:

$$K_w = \frac{[C_{\text{H}_3\text{O}^+,core}][C_{\text{OH}^-,core}]}{[C_{total \text{H}_2\text{O},core}^2]} \quad (2.16)$$

$$K_{eq1} = \frac{[C_{\text{HCO}_3^-,core}][C_{\text{H}_3\text{O}^+,core}]}{[C_{\text{CO}_2,core}^*][C_{total \text{H}_2\text{O},core}]^2} \quad (2.17)$$

$$K_{eq2} = \frac{[C_{\text{CO}_3^{2-},core}][C_{\text{H}_3\text{O}^+,core}]}{[C_{\text{HCO}_3^-,core}][C_{total \text{H}_2\text{O},core}]} \quad (2.18)$$

The vapor-liquid equilibrium for CO_2 and H_2O at the shell/core interface is described using

$$\phi_{\text{CO}_2} P y_{\text{CO}_2,int} = H_{e\text{CO}_2} \gamma_{\text{CO}_2} x_{\text{CO}_2,int} \quad (2.19)$$

$$\phi_{\text{H}_2\text{O}} P y_{\text{H}_2\text{O},int} = x_{\text{H}_2\text{O},int} \gamma_{\text{H}_2\text{O}} f_{\text{H}_2\text{O}} \quad (2.20)$$

The fugacity coefficients for CO₂ and H₂O are obtained using SRK model while the activity coefficients are obtained using the eNRTL model as noted earlier. Henry's law constants for sodium carbonate solutions are obtained from the literature [24].

2.3.2. VLE model validation. The VLE model developed for Na₂CO₃-CO₂-H₂O system is validated with the limited data available in the open literature [24]. Figure 2.2 compares the model results with the experimental data for 10 wt% solvent at 40°C and 80°C. Figure 2.2 shows the change in CO₂ loading with increase in the partial pressure of CO₂. The model can be further improved by obtaining the data at lower CO₂ loadings, high sodium carbonate concentrations, and for a wider temperature range.

Figure 2.2. VLE model validation for 10 wt% Na₂CO₃ capsules.

Figure 2.3. Heat of absorption for 10 wt% Na₂CO₃ solution.

2.3.3. Heat of absorption. The heat of absorption data for Na₂CO₃-CO₂-H₂O system is scarce in the literature. The literature review yielded only one value for heat of absorption at 25°C reported by Berg et al. [25]. The heat of absorption as a function of temperature and CO₂ loading is calculated using the enthalpy model presented earlier. Gao et al. [26] reported the heat of absorption for K₂CO₃ solvent system. The heat of absorption trend shown in the Figure 2.3 agrees qualitatively with potassium carbonate solvent reported in the literature [26]. It can be seen from the figure using a constant value underestimates the heat of absorption at lower loadings and overestimates at higher loadings. Therefore, capturing the nonlinearity in the heat of absorption is critical especially for contactors like fixed beds where there is considerable temporal and/or spatial variation of CO₂ loading.

2.3.4. Model of a single microcapsule. The fundamental heat and mass transfer mechanisms in developing a reactor scale model differs in comparison to the microcapsule level model. The different mechanisms occurring at a microcapsule level are captured with the help of a single microcapsule model. The microcapsule in this study is modeled as two distinct components, solvent as the core and a solid polymer encapsulating the solvent. Figure 2.4 shows the schematic of a single microcapsule. The following assumptions are made while developing the capsule model: (1) all capsules are perfectly spherical, (2) there is no accumulation within the shell wall,

- (3) the core fluid is well mixed, (4) mass transfer through the shell is only through diffusion, and (5) there is no loss of the solvent through the membrane.

Figure 2.4. Schematic of microcapsule showing shell and core components.

Table 2.2. Mass and energy balance equations for the microcapsule.

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{i,shell} r^2 \frac{\partial C_{i,shell}}{\partial r} \right) = 0 \quad (2.21)$$

$$\frac{d(C_{i,core})}{dt} = a_e N_{i,L} \quad (2.22)$$

$$\frac{d(C_{Na_2CO_3,core})}{dt} = 0 \quad (2.23)$$

$$\rho_{shell} C_{p,shell} \frac{\partial T_s}{\partial t} = K_{shell} \left(\frac{2}{r} \frac{\partial T_s}{\partial r} + \frac{\partial^2 T_s}{\partial r^2} \right) \quad (2.24)$$

$$\frac{\partial (C_{T,L} H_L)}{\partial t} = h_c a_e (T_s - T_c) + a_e N_{CO_2,L} \bar{H}_{CO_2,L} + a_e N_{H_2O,L} \Delta H_{vap} \quad (2.25)$$

Table 2.2 presents the basis structure of mass and energy balance equations of the capsule. These constitutive equations are modified, wherever necessary, based on the capsule interactions with the surrounding, for example in the case of a moving bed and bubbling fluidized beds the solids can interact with the reactor internals (embedded heat exchanger) if any. The corresponding boundary conditions for the microcapsule model can be found in Appendix A.

2.3.5. Model of the experimental system. In the experimental system described in Section 2.2, mass transfer takes place from the stationary gas to the static capsules. The experimental

characterization of capsules absorbing CO₂ is carried out at isothermal conditions for temperatures 25°C, 40°C, and 60°C. The following correlations are used for the liquid and gas phase mass transfer coefficients [27,28] for a static spherical particle. The CO₂ diffusion coefficient through the polymer shell is estimated using the experimental data.

$$\frac{k_{i,L}d_{core}}{D_{i,L}} = \frac{2\pi^2}{3} \quad (2.26)$$

$$\frac{k_{i,G}d_{cap}}{D_{i,G}} = 2 + 0.6 \left(\frac{d_{cap}^3 \Delta \rho g}{\rho_G \mu_G^2} \right)^{\frac{1}{4}} \left(\frac{\mu_G}{D_{i,G}} \right)^{\frac{1}{3}} \quad (2.27)$$

The overall mass balance equation for the gas phase present in the experimental reactor described earlier is given by

$$\frac{dC_{Gbulk,R}}{dt} = - \frac{n_{cap}(N_{surf}A_{cap})}{V_R} \quad (2.28)$$

where $C_{Gbulk,R}$ is the total gas phase concentration in the reaction chamber V_R .

2.4. Parameter Estimation and Data Reconciliation

The experimental data obtained for three different temperatures using the setup shown in section 2.2 is used in the estimation framework presented here. The solvent is encapsulated inside the microcapsule resulting in a challenge with respect to knowing the solvent concentration after the encapsulation. The diffusivity parameter in the capsule mass transfer model, $D_{i,shell}$ in eq. (2.29) needs to be estimated. The parameter $D_{i,shell}$ is given by

$$D_{i,shell} = C_{i,1} \exp\left(-\frac{C_{i,2}}{T}\right) \quad (2.29)$$

Furthermore, even though a good guess of the initial solvent concentration in the microcapsule, $C_{Na_2CO_3,core}|_{t=0}$, is available, an exact value at the beginning of the experiment is not available as the concentration of the encapsulated solvent is practically impossible to measure and therefore should be reconciled. The log-likelihood objective function considered for parameter estimation is

$$\max_{C_1, C_2, C_{Na_2CO_3, core}|_{t=0}} \left\{ -\frac{1}{2} \sum_{i=1}^{Nmeas} \left(n_i \log(2\pi + 1) + n_i \log \left[\frac{1}{n_i} \sum_{j=1}^{NDyn} \sum_{k=1}^{M_{ij}} w_j^2 \frac{(Z_e(t_{ijk}) - Z_m(t_{ijk}))^2}{Z_{m,ijk}^{Y_i}} \right] \right) \right. \\ \left. + \theta_i \sum_{j=1}^{NDyn} \sum_{k=1}^{M_{ij}} \log w_j Z(t_{ijk}) \right\}$$

The number of unique variables that are measured over all experiments is denoted as $Nmeas$. The term $w_j^2 \frac{(Z_e(t_{ijk}) - Z_m(t_{ijk}))^2}{Z_{m,ijk}^{Y_i}}$ is the weighted modeling error calculated for all the dynamic experiments, in which Z_m denotes the value of the measured variable, and Z_e represents the corresponding value calculated from the model. The term θ_i is a heteroscedasticity parameter that is used to account for the standard error of the observations. This value is automatically calculated during the maximization of the log likelihood function. The optimization problem is solved using sequential quadratic programming (SQP) in Aspen Custom Modeler (ACM).

2.5. Microcapsule Model Validation

The CO₂ diffusivity parameters within the PDMS shell wall are estimated. The initial solvent concentration in microcapsules presents an uncertainty about the state of core solvent inside the shell. Table 2.3 presents the estimated parameters and reconciled initial solvent concentration along with their corresponding lower and upper bounds. The microcapsule model is validated using the estimated parameters and reconciled initial solvent concentration against the experimental data. Figure 2.5 compares the model results for the transients in the total gas pressure with the experimental data at 25°C, 40°C, and 60°C. It can be seen that the model results match very well with the experimental data.

Table 2.3 Estimated model parameters and reconciled variables

Temperature	Parameter/ Variable	Estimated/ reconciled value	Lower bound	Upper bound	Units	Std. deviation	Initial value
	C_1	2.153e-8	1e-8	1e-5	[m ² /s]	4.6e-10	2.5e-8
	C_2	1106	1000	2500	[K]	6.7	1200
25°C	Solvent concentration	7.8	5	12	wt%	0.003	10
40°C		7.6	5	12	wt%	0.002	10
60°C		6.2	5	12	wt%	0.002	10

Figure 2.5 Comparison between the model results and the experimental data for the transients in the reactor chamber pressure at 25°C, 40°C, and 60°C.

2.6. Conclusions

A rigorous microcapsule model with sodium carbonate as the encapsulated solvent is developed. The vapor liquid equilibrium predictions from the model are validated with the literature data. The heat of absorption of CO₂ with sodium carbonate solvent is compared to the extremely limited data in the literature. It is identified that the need for more heat of absorption data that can further improve the insights from the analysis when scale up studies are done. The diffusion coefficient of CO₂ through the PDMS has been estimated using the experimental data shared by LLNL. The initial solvent concentration is reconciled to account for the uncertainty in the state of encapsulated solvent. Finally, the capsule model predictions are compared to the experimental data and the results provide the confidence to conduct scale up studies. However, more data with the combinations of different solvent weight percentages, temperatures can be useful to characterize the capsules.

Chapter 3. Fixed Bed Modeling of MECS

The rigorous capsule model described in the chapter 2 will be used to perform the scale up studies of MECS. Fixed bed configuration for MECS technology using sodium carbonate solvent will be presented in this chapter.

3.1. Introduction

Fixed bed reactors are well studied in the literature due to their application in the petroleum industry [29]. Fixed bed systems are simple to operate, easy to scale up, and offer low sorbent attrition. Several mathematical models of fixed bed reactor describing gas-solid interaction have been published in the literature [30]. However, the MECS has both solid and liquid components in the form of polymer and encapsulated solvent representing a single particle. Therefore, the fixed bed configuration containing MECS involves interaction between gas, solid and a liquid phase. To accurately resolve the microscale behavior, the capsule model presented in chapter 2 is integrated with the bulk phase modeling equations of the fixed bed. In addition, both the absorption and regeneration stages of the fixed bed process is simulated in this work to understand the economic and operational aspects of MECS technology. Lawrence Livermore group [23] developed a simplified carbonate capsule model to estimate the sizes and energy penalties of both fixed bed and fluidized bed absorbers. The authors assumed isothermal conditions in the fixed bed reactor, which may not be possible considering the CO₂ absorption and water movement between the flue gas and capsules. Hornbostel et al. [23] also made simplifying assumptions about the regeneration process (e.g., assuming a constant heat of reaction, fixing the regeneration time at 10 minutes) due to a lack of experimental data on the regeneration process. The authors also did not account for water flux across the capsule shell, which is a critical aspect of carbonate capsule performance. However, detailed modeling of fixed bed reactors for MECS and techno-economic analysis (TEA) of these systems for CO₂ capture is lacking in the current literature.

The contribution through this work adds onto the MECS reactor modeling performed by Hornbostel et al. [23] by considering detailed reactions, water flux, and temperature variation to accurately resolve the performance of carbonate MECS in a fixed bed reactor. The purpose of this modeling work is also to evaluate the commercial feasibility of MECS in a fixed bed configuration

for CO₂ capture. Therefore, a techno-economic analysis (TEA) is performed here for a range of materials and operating parameters, and the results are compared to the state-of-the-art MEA carbon capture technology. Raksajati et al. [14] performed a TEA on both fixed and fluidized beds of MECS filled with MEA instead of carbonate solution. That group made some simplifying assumptions, e.g., lumping mass transfer resistances and assuming uniform loading throughout the fixed bed. These assumptions may be reasonable for MEA capsules, but they would break down for carbonate capsules, which absorb CO₂ slowly. Therefore, detailed mass transfer and heat transfer models are incorporated into our TEA work to study the performance of carbonate capsules in a fixed bed configuration. The first principles based dynamic fixed bed model proposed here not only accounts for the interaction between capsule model, bulk gas phase, but also with the embedded heat exchanger which is a novelty of this work as opposed to the previous works in this area [14,23]. The fixed bed model also accounts for the water dynamics in the capsule as H₂O can also permeate through the shell. This aspect of the MECS in a fixed bed configuration has not been addressed in the previous studies. The multi scale fixed bed model discretized in both time and spatial domain is implemented in an equation-oriented modeling framework available in Aspen Custom Modeler (ACM). The fixed bed operation is a cyclic process switching between absorption and regeneration stages which makes it difficult to simulate as the capsules state at the end of absorption process is the initial capsule state for starting the regeneration process. In other words, one needs to ensure that fixed model simulating absorption and regeneration has reached cyclic steady state. Another challenge stems from having different boundary conditions between absorption and regeneration stages as it can introduce convergence issues in solving the complete cycle. The cyclic steady state is ensured in the current implementation with the help of a flowsheet level constraints on the capsules state and using automation framework in ACM.

3.2. Modeling of a Fixed Bed Reactor

The reactor configuration explored in this chapter is a fixed bed temperature swing absorption with the combination of both direct and indirect heating approach as shown in the Figure 3.1. The direct heating approach for regeneration, where a hot steam is directly injected into the bed as shown in Figure 3.1(b), is widely used for temperature swing adsorption. Since a CO₂-rich stream is desired for sequestration, typically steam is injected as it can be easily condensed from the stream exiting

the desorber. However, since steam cannot be condensed in a fixed bed system containing MECS, only the sensible heat from the steam is available for heating thus a large amount of steam will be needed to regenerate the encapsulated chemical solvent, if the entire amount of heat has to be provided by the injected steam.

Figure 3.1 Schematic of fixed bed configuration for MECS showing (a) absorption stage, (b) regeneration stage.

The indirect heating approach, where the heat is provided by an embedded heat exchanger through which steam or some other hot utility can be sent, can be helpful in solving the issues mentioned above [31-33]. However, the direct injection of the steam has the advantage that other than heating, it also reduces the partial pressure of CO₂ in the system thus reducing the temperature required to regenerate the solvent to a certain loading. Furthermore, due to the presence of steam, water loss from the solvent inside the capsule can be greatly reduced. Therefore, both direct heating through injection of steam to the bed as well as indirect heating by condensing steam in an embedded heat exchanger are considered.

The fixed bed model developed here has three phases- the gas phase that enters the fixed bed as feed, the solid phase constituting the polymer shell, and the liquid phase i.e., the absorbing liquid present inside the polymer shell. The assumptions made in the modeling of the fixed bed are: (1) the gas behavior is assumed to follow SRK equation of state, (2) only axial variation of the transport variables corresponding to the bulk phase is considered, (3) pressure drop follows the

Ergun equation, (4) the embedded heat exchanger is assumed to have a triangular pitch arrangement for the tubes. The heat and mass transfer correlations along with the boundary conditions used in the model are provided under the supporting information.

Mass balance

Gas Phase

$$\epsilon_{bed} \frac{\partial C_{i,G}}{\partial t} = -\frac{\partial(u_G C_{i,G})}{\partial z} - (1 - \epsilon_{bed}) a_{e,cap} N_{i,G} \quad (3.1)$$

Energy balance

Gas Phase

$$\begin{aligned} \epsilon_{bed} \frac{\partial(C_{T,G} H_G)}{\partial t} = & -\frac{\partial(u_G C_{T,G} H_G)}{\partial z} - (1 - \epsilon_{bed}) a_{e,cap} (N_{CO_2,G} \bar{H}_{CO_2,G} + N_{H_2O,G} \bar{H}_{H_2O,G}) \\ & - (1 - \epsilon_{bed}) a_{e,cap} h_{gs} (T_g - T_s) + a_{e,hx} h_{hxwG} (T_{hxw} - T_g) \end{aligned} \quad (3.2)$$

Heat exchanger tube wall

$$\rho_{hxw} C_{p,hxw} \frac{\partial T_{hxw}}{\partial t} = a_{e,hx} h_{hxw} (T_{sat} - T_{hxw}) - a_{e,hx} h_{hxwG} (T_{hxw} - T_g) + K_{hxw} \frac{\partial^2 T_{hxw}}{\partial z^2} \quad (3.3)$$

Pressure Drop (Ergun Equation)

$$\frac{\partial P}{\partial z} = - \left\{ \frac{150 \mu_g (1 - \epsilon_{bed})^2}{d_{cap}^2 \epsilon_{bed}^3} u_G + \frac{1.75 \rho_g (1 - \epsilon_{bed})}{d_{cap} \epsilon_{bed}^3} u_G^2 \right\} \quad (3.4)$$

A commercial-scale post-combustion CO₂ capture process is considered for the flue gas from a 644 MWe gross power subcritical pulverized coal power plant. Due to constraints on the maximum column sizes and the large volume of flue gas produced from this power plant, multiple fixed bed reactors in parallel are required as shown in Figure 3.2. At any instant of time, there are some beds undergoing absorption while some undergoing desorption. The bed size in Table 3.1 is based on heuristics, economics, and pressure drop calculations. A smaller diameter bed can lead to lower bed capacity and thus large number of beds. A larger diameter bed can lead to lower number of beds and thus improve process economics but can lead to non-uniform gas distribution and practical issues in terms of construction and transportation to site. A 15-m diameter bed is assumed to be practical. The height of the bed is limited by the affordable pressure drop in the bed. The studies presented here correspond to Case 11B in the NETL baseline study [34]. The flue gas contains 13 mol% CO₂, 15 mol% H₂O, and 72 mol% N₂. The flue gas at the inlet of absorbers is assumed to be saturated with water since the flue gas typically passes through a scrubber before the capture system.

Figure 3.2 Simplified schematic representation of the commercial-scale MECS fixed bed TSA process.

For calculating the breakthrough time, it is important to define the term breakthrough time first. It is expected that for CO₂ capture applications, there would not be any target for achieving an instantaneous CO₂ capture, rather an integral capture target over a period of time. Also, for a fixed bed, as the bed is taken in line, there is practically no CO₂ slip from the bed for some time. Therefore, if there is an overall target of 90% CO₂ capture, when the breakthrough takes place, the capture may be lower than 90%. With these considerations, the breakthrough time is defined in this work as the maximum allowable time at which the integral CO₂ slip (i.e., CO₂ slip from the time the bed comes online for absorption to the breakthrough time) reaches 10% of the total adsorbate that has been fed to the fixed bed over that period of time. The breakthrough time (t_b) is calculated using the equation:

$$F_{in} z_{CO_2, in} 0.1 t_b = \int_{t_0}^{t_0+t_b} F_{out} z_{CO_2, out} dt \quad (3.5)$$

where F_{in} is total molar flow into the bed, $z_{CO_2, in}$, and $z_{CO_2, out}$ are the inlet and outlet mole fractions of CO₂. The breakthrough time (t_b) depends mainly on the solvent under consideration and on the residence time of flue gas in the reactor. The effect of residence time on the key characteristics of a fixed bed reactor such as absorption time (breakthrough time), regeneration time, and number of beds in the cycle is analyzed. Later, the sensitivity of capital and operating cost of the fixed bed reactor with respect to residence time is also presented. The important design and operating variables in this analysis are listed in Table 3.1.

Table 3.1 Key variables for the commercial-scale fixed bed design

Absorption Stage	Value	UOM
Length of the bed	10	m
Diameter of the bed	15	m
Outlet gas pressure	1.0	bar
Solvent concentration	20	wt%
Desorption Stage		
Inlet steam temperature	130	°C
Steam residence time	100	s
Specific area for indirect heating	117	m ² /m ³
Average loading at the end of cycle	0.1	mol HCO ₃ ⁻ /mol Na ⁺

3.3. Fixed Bed Results

The impact of major operating variables on regeneration energy and economics of the MECS have been investigated. The variables examined are the flue gas residence time, initial bed temperature, heat recovery, and reaction rate. The absorption rate of CO₂ in the carbonate solutions can be enhanced using a catalyst. In all the studies presented here, the capsules are filled with sodium carbonate solution without any catalyst unless specified otherwise. The regeneration temperature for all the studies reported in the fixed bed studies ranges between 105°C-115°C, which is below the solvent degradation temperature. The techno- economic analysis on MECS is performed considering two different materials of construction for fixed bed reactor. The results of the study are compared to standard MEA technology.

3.3.1. Impact of residence time. One of the key design variables for fixed beds is the residence time of reactants in a bed, which is a function of the bed diameter, height, and the flowrate through it. A higher residence time can help to obtain higher volume-averaged loading that is closer to the equilibrium loading. A higher residence time will also result in longer breakthrough time and lower energy penalty. These two aspects are analyzed in detail later. However, since the bed height is limited because of pressure drop constraints, a higher residence time can only be obtained by decreasing the flowrate or increasing the bed diameter, or by both. It should be noted that decreasing flowrate would lead to higher number of beds in parallel to process the total amount of the flue gas from the power plant. Thus, any of the options noted above will lead to a larger total cross-sectional area, which leads to higher total reactor volume and therefore higher capital cost.

Therefore, the tradeoffs between the capital costs and operating costs need to be investigated to obtain the optimal residence time.

While the parameters for the diffusivity of CO₂ through the shell could be obtained by using the experimental data as noted earlier, we currently do not have in-house mass transfer data for H₂O through the shell. The shell diffusivity parameter for water is taken from the open literature for poly (dimethylsiloxane) material [35]. Table 3.2 shows the effect of residence time on the key variables such as the breakthrough time (or absorption time), desorption time and total number of beds required in the cycle when the initial bed temperature is 40°C. Since the outgoing clean flue gas from the capture system goes to the stack, the outlet pressure from the bed is specified to be 1 bar. Therefore, as the operating conditions are changed, the bed inlet pressure changes depending on the pressure drop through the bed that is calculated by the Ergun equation as mentioned earlier. The total number of beds is determined by solving a scheduling problem that ensures the required number of parallel beds for absorption is always available. As expected, with the increase in residence time, i.e., decrease in the superficial velocity, the breakthrough time keeps increasing and the number of beds in parallel under absorption keeps increasing. Since higher breakthrough time indicates higher loading of the capsules, correspondingly it takes a longer time to regenerate the bed. When the absorption and desorption times are similar, the number of beds undergoing absorption is similar to the number of beds undergoing desorption as expected. On the other hand, when the breakthrough time is much shorter than desorption time, for example when τ is 75 s, the number of beds in absorption cycle is much less than the number of beds in desorption cycle. However, the number of beds undergoing desorption decreases as the breakthrough time increases.

Table 3.2 Impact of residence time on the number of beds and cycle times

Residence time (τ) (s)	Breakthrough time (t_b) (s)	Desorption time (s)	Absorption beds	Total beds in the cycle
75	922	3425	25	118
100	2765	4223	38	97
150	6723	4495	67	112
200	10362	4518	96	138

The breakthrough curves and capsule loadings are shown in Figures 3.3 and 3.4, respectively, at different sections of the bed for two different residence times of the flue gas. For a fair comparison, the initial CO₂ loading of the capsules is specified to be zero for the results shown in Figures 3.3 and 3.4. It can be observed in Figure 3.3 that the outlet concentration at the breakthrough time for

the bed with higher residence time is higher than the bed with the lower residence time. The reason becomes clear by considering the definition of the breakthrough time given by Eq. (3.5), which is based on the integral CO_2 slip, and by comparing the exit concentration profiles corresponding to the higher and lower residence times. Figure 3.4 shows the CO_2 loadings in the capsules at different nodes along the length of the bed. As mentioned earlier, the breakthrough time increases with increase in flue gas residence time in the fixed bed. Therefore, given the same initial bed temperature, the average CO_2 loading is more for higher flue gas residence time.

Figure 3.3 Breakthrough curve for different residence times at different locations: (1) entrance, (2) middle, (3) end of the bed (Note: solid lines in black color correspond to residence times of 75 s while dash-dot lines in orange color correspond to residence times of 100 s).

This study shows that there is an optimum number of beds or minimum total volume of the bed corresponding to an optimal residence time. It should be noted that a decrease in the residence time or an increase in the superficial velocity results in an increase in the inlet pressure of the flue gas and the pressure drop through the bed as the outlet pressure remains fixed at 1 bar. Obviously, the maximum inlet pressure is observed for the lower residence time (high superficial velocity) and vice versa. When the operating range for superficial velocity varies from 42 s to 200 s, the inlet pressures change between 3.25 bar to 1.2 bar. The increase in the pressure helps to improve the loading, but at the cost of a blower, the capital and operating costs of which needs to be considered.

Thus, the optimization needs to be done with due consideration of the capital and operating costs of the entire system as presented later in this work.

Figure 3.4 CO₂ loading comparison for different residence times at different locations: (1) entrance, (2) middle, (3) end of the bed (Note: solid lines in black color correspond to residence times of 75 s while dash-dot lines in orange color correspond to residence times of 100 s).

3.3.2. Impact of initial bed temperature. An increase in the flue gas temperature and the bed temperature increases the rate of reaction but adversely affect the equilibrium CO₂ loadings. In addition, as the flue gas is saturated with water, a higher temperature leads to higher mass flowrate through the system leading to a decrease in the residence time. Figure 3.5 shows the sensitivity of the total bed volume for different initial bed temperatures. It is observed that when the residence time is lower, a higher bed temperature is advantageous due to the improvement of the reaction rate. However, as the residence time increases, the number of parallel beds undergoing absorption increases to a larger degree at higher temperatures when compared to the same residence time increase at lower temperature. This is due to the higher mass flowrate as mentioned above thus leading to a steeper increase in the bed volume at higher temperature.

Figure 3.5 Impact of the residence time on the total volume of the beds at various initial bed temperatures.

The bed temperature also affects the regeneration duty. The regeneration duty for the system under consideration is mainly due to sensible heat required for the capsules, desorption heat for CO_2 , and heat of vaporization as modeled in section 2.3. Figure 3.6 shows the effect of residence time on the regeneration duty for varying bed temperatures. The regeneration energy keeps monotonically decreasing with higher residence time as the sensible heat/total heat ratio keeps decreasing. An increase in absorption temperature reduces the temperature difference between absorption and desorption cycles, which, in turn, reduces the amount of sensible heat required for raising the temperature of the capsules and the solvent to the stripper temperature. However, the total volume of the beds undergoing regeneration must also be taken into consideration. It is observed that the regeneration energy requirement increases considerably if the bed temperature is at 40°C , and residence time is less than about 100 s. For 40°C when the residence time decreases below 100 s, there is a substantial increase in the bed volume as shown in Fig.3.5. In addition, the relative difference in temperature between the absorption and desorption conditions is the highest for this case. These two effects result in a very high regeneration energy requirement. As the residence time increases, the regeneration energy requirement becomes lower for 40°C in comparison to 60°C and 80°C because of higher CO_2 loading at 40°C .

Figure 3.6 Impact of the residence time on the regeneration duty for various initial bed temperatures.

3.3.3. Impact of the reaction rate. The reaction of carbonate solutions with CO₂ is slow and can be promoted in the presence of a catalyst [19,36]. Nathalie et al. [36] studied the absorption of CO₂ in the aqueous sodium carbonate solution with and without carbonic anhydrase. The results showed that the presence of carbonic anhydrase catalyst in the carbonate solutions enhances the reaction rate of CO₂ with solvent approximately by 10 times. Therefore, the effect of reaction rate on the performance of fixed bed operation is analyzed. In the first case denoted as normal rate, the reaction rate is for an uncatalyzed solvent as presented before. In the other case here, denoted as '10 x normal rate', it is assumed that the catalyst can enhance the reaction rate by 10 times the 'normal rate' at all operating conditions. Regeneration duties along with other key parameters for both the cases and for both the residence times studied above are shown in Table 3.3. It can be noted that the case with larger residence time has lower energy requirement. The relative difference between the total volumes required for both residence times decreases as the reaction rate is increased. This analysis shows that the presence of a catalyst and a longer residence time i.e., a lower superficial velocity to the bed is beneficial. However, lower inlet superficial velocities increase the parallel number of beds operating in a cycle that leads to a higher capital cost. Therefore, one should consider a techno-economic analysis including both capital and operating costs in determining the optimum residence time. The results of such an analysis are presented in the ensuing sub-section.

Table 3.3 Key parameters showing energy and volume requirements for MECS in a fixed bed configuration

Variable	Normal rate		10 x normal rate	
	$\tau = 75\text{ s}$	$\tau = 100\text{ s}$	$\tau = 75\text{ s}$	$\tau = 100\text{ s}$
Absorption time	922	2765	2211	4053
Desorption time	3425	4223	4292	4432
Total beds in the cycle	118	97	74	80
Total Volume (m ³)	208523	171413	130768	141371
Regeneration duty (GJ/tCO ₂)	150	35	36	17

3.3.4. Impact of heat recovery. The regeneration energy values shown in Table 3.3 are much higher than MEA which typically varies from 3.4-4.3 MJ/kg CO₂ [37]. Heat recovery can play a major role in reducing the overall energy penalty for regeneration. As mentioned earlier, the heat required during desorption stage can be delivered via two methods, direct heating, and indirect heating. These methods can be provided alone or can be combined. Direct heating can be achieved by injecting steam into the bed. This method has the advantage that it also reduces the partial pressure of CO₂ thus a lower loading can be obtained even at a lower temperature. The main disadvantage is that since steam condensation external to the capsule is not desired, only very little heating duty can be obtained from the steam depending on the available superheat in the inlet steam and thus a large amount of steam will be required for providing the heat of desorption. Indirect heating is provided through steam condensation in an embedded heat exchanger. Indirect heating has the advantage of reduced steam consumption in comparison to direct heating. Its disadvantage is that a larger contactor size is needed due to the presence of the embedded heat exchanger. If only indirect heating is considered, CO₂ partial pressure in the bed will be high leading to a higher regeneration temperature than direct heating for a given desired loading from the regeneration cycle. Therefore, the likely optimal configuration will be a combination of direct and indirect heating methods to exploit the advantage of each of the methods. During absorption, the flue gas flow direction is downward. Obviously, at the time of breakthrough, the bed loading keeps decreasing from the top towards the bottom. During desorption, if the steam flow direction is downward, then as CO₂ concentration in the outgoing gas keeps increasing on the flow direction, CO₂ can get reabsorbed in the downstream capsules that have lower loading. To circumvent this issue, the flow direction during desorption is considered opposite to the flow direction during absorption.

Heat recovery methods are not modeled in this study; instead, sensitivities with respect to a few discrete values have been evaluated. It has been assumed that there are no physical or chemical changes in the system due to heat recovery. In a conventional stripper for MEA, the sensible heat recovered from the liquid outlet stream for about 5°C temperature approach using a cross heat exchanger is about 80-90%. Raksajati et al. [14] assumed 60% of total sensible heat duty can be recovered in their fixed bed studies for microencapsulation of MEA. This is based on the process scheme used in the dehydration unit of a natural gas processing plant. Figure 3.7 shows the variation of total regeneration duty with residence time for different extents of heat recovery for initial bed temperature of 40°C. The number of beds at any point undergoing desorption decreases and at the same time, the amount of CO₂ absorbed by the microcapsules increases with the increase in residence time. Overall, this reduces the total regeneration energy with the increase in the residence time as shown in Figure 3.7. It can be observed in Figure 3.7 that the heat recovery and residence time plays an important role to make the regeneration duty comparable to the MEA.

Figure 3.7 Impact of the residence time on regeneration duty for different extents of heat recovery.

3.4. Techno-Economic Analysis

For novel systems like MECS, there is lack of information in the existing literature. The techno-economic analysis presented here is conducted by considering the capital/material costs including

capsule cost (both shell and the solvent), fixed bed with embedded heat exchanger, and compressor costs. The capital cost used here is the bare module cost, irrespective of whether the purchased cost is calculated using Aspen Process Economic Analyzer[®] (for C-steel reactor, heat exchanger, and compressor) or spreadsheet (concrete reactors). In this approach, starting with the purchased cost, additional direct expenses such as material and labor for installation as well as indirect expenses such as the freight insurance, taxes, construction overhead, and contractor engineering expenses are included [38]. In calculating operating expenses, the cost of direct and indirect steam utilized for the regeneration of CO₂ as well as the cost of power in the compressor have been included. Since there is no information about the capital costs for MECS in the literature, especially the costs of capsules and reactor with an embedded heat exchanger, the effect of +/-50% uncertainty in the capital cost is evaluated and presented in section 3.4.2.

The cost of the capsules including the solvent and the shell material is calculated using internal data as shown in Table 3.4. The fixed bed configuration has an embedded heat exchanger which is represented in APEA[®] as a shell and tube heat exchanger to calculate the capital cost. However, the size of the exchanger is larger than the maximum size available in APEA[®]. Therefore, the purchased cost is first obtained from the APEA[®] for the maximum size of the heat exchanger. Then the cost of the heat exchanger corresponding to the actual embedded heat exchanger is calculated using Eq. (3.6).

$$Estimated\ cost = Base\ cost \left(\frac{required\ area}{base\ area} \right)^{0.6} \quad (3.6)$$

The capital cost for the contactor made from concrete is performed using some internal information that includes material, direct and indirect costs which are shown in the Table 3.4. The internal wall-to-floor area and roof area are used in the capacity scaling to find the capital cost of a single bed is done by applying Eq. (3.6). The cost of heat exchanger tubes embedded in the concrete exchanger is calculated using APEA[®]. The inlet flue gas is compressed to meet the pressure drop requirements of the fixed bed reactor. The capital cost for the compressors is obtained using APEA[®]. The operating cost required for the compressors is calculated using the power needed to achieve the required compression. The cost of the low-pressure process steam is taken from Turton et al. [38] to calculate the operating cost.

Table 3.4 Unit prices used in the capital cost estimation of concrete and capsules

	Cost	Basis	Source
Concrete	2174 (\$/m ²)	Internal wall to floor area	(Rochelle, 2018) [39]
Capsule	0.0593 (\$/kg)	Mass of capsules	(Stolaroff, 2018) [40]

The equivalent annual operating cost (EAO) is calculated by adding the annualized capital cost to the yearly operating cost (YOC) [38] using Eq. (3.7). The annualized capital cost is obtained by amortizing the total capital cost over the period of plant life. The discount rate is assumed to be 10% and the operating life for the reactors and compressors, is assumed to be 10 years and 2 years for the capsules. The TEA of the MECS system is compared with that of conventional MEA-based CO₂ capture in towers. For the MEA system, capital and operating costs are obtained from Case 11B in the National Energy Technology Laboratory (NETL) baseline study [34].

$$EAO = Capital\ cost \frac{i}{(1 - (1 + i)^{-n})} + YOC \quad (3.7)$$

where i is the discount rate, and n is the number of operating years. The studies presented in the earlier sections point to various design parameters and operating conditions that can improve the economics of the MECS system, but also show the strong tradeoff between the capital and operating costs as those design parameters and operating conditions are varied. Therefore, a techno-economic study is undertaken. Equivalent annual operating cost (EAO) is considered as the economic measure for this study. Two different materials of construction, carbon-steel and concrete are considered for the absorber/desorber.

3.4.1. Impact of residence time and initial bed temperature. The impact of the residence time on the capital cost is analyzed for three different initial bed temperatures, 40°C, 60°C, and 80°C. As shown in Table 5, the number of beds goes through a minimum with increase in residence time. But the regeneration energy keeps decreasing as shown in Figures 3.6 and 3.7. Figures 3.8 and 3.9 shows the annualized capital cost for concrete and carbon-steel respectively. The steeper increase in the annualized capital cost for the initial bed temperature of 80°C is expected since Figure 3.5 shows the steep increase in the bed volume with the residence time for the initial bed temperature of 80°C and the capital cost is positively correlated to the bed volume. Figures 3.8 and 3.9 also show the annualized capital cost for the MEA system using packed absorber and strippers, which is found to be considerably lower than the MECS system operating with carbonate

solvent in a fixed bed reactor. The capital cost for concrete based reactor is lower compared to reactor made using carbon-steel.

Figure 3.8 Impact of residence time on EAO for different initial bed temperatures with concrete as the material of construction for the beds.

Figure 3.9 Impact of the residence time on the annualized capital cost for various initial bed temperatures with carbon steel as the material of construction for the beds.

The optimum EAO value depends on the amount of heat recovery that can be achieved and also on the type of material used for contactor construction. As mentioned earlier, the sensible heat

recovered from the liquid outlet stream in the case of MEA for 5°C temperature approach is about 80-90%. Thus, it is desired to compare the case when the heat recovery is similar to MEA. This study is conducted assuming a heat recovery of 85%, which is considered to be the best-case scenario. It should be noted that such a high extent of heat recovery can be very difficult to achieve, if not impossible, for fixed beds and the authors by no means indicate the feasibility of such high extent of heat recovery. Figures 3.10 and 3.11 show the EAOE for varying residence time at different initial bed temperatures for concrete and carbon steel as the material of construction, respectively. The EAOE for the MEA system is also shown in both the figures. In Figure 3.10, it can be observed that the optimal initial bed temperature is 60°C and the minimum EAOE for the MECS system with the concrete contactor is approximately 1.8 times higher than the MEA technology. Figure 3.11 shows that the minimum EAOE that corresponds to the initial bed temperature of 60°C is approximately 2.7 times that for the MEA technology. The EAOE values for both concrete and carbon-steel with a range of heat recovery percentages are listed in the Appendix B.

Figure 3.10 Impact of the residence time on EAOE for 85% heat recovery for concrete contactors at various initial bed temperatures.

Figure 3.11 Impact of the residence time on EAO for 85% heat recovery for carbon steel contactors at various initial bed temperatures.

3.4.2. Uncertainty analysis. Since there is no capital cost data available for these systems from real life, there can be high uncertainty in the capital cost estimates. EAO values with +50% uncertainty in the carbon steel contactor cost and -50% uncertainty in the concrete contactor cost is evaluated since they serve as upper and lower bounds, respectively. Figures 3.12 and 3.13 show the EAO for 60% and 85% heat recovery, respectively, when the initial bed temperature is 60°C. It is observed that the uncertainty in the capital cost estimation and the extent of heat recovery can have considerable impact on the optimum EOAC value. Obviously, -50% uncertainty in the concrete contactor cost leads to the minimum EAO for both 60% and 85% heat recovery. Even with consideration of uncertainty, the minimum EAO for 60% heat recovery is about 2.5 times higher than the MEA technology whereas for 85% heat recovery the minimum EAO value is 1.5 times of the MEA technology. However, as noted earlier, achieving such a high extent of heat recovery in a fixed bed system would be difficult. The 10X rate did not offer much improvement in the EOAC values as shown in Figures 3.12 and 3.13.

Figure 3.12 Impact of residence time on EAOE by considering uncertainty in the capital cost (60% heat recovery) for the initial bed temperature at 60°C.

Figure 3.13 Impact of residence time on EAOE by considering uncertainty in the capital cost (85% heat recovery) for the initial bed temperature at 60°C.

3.5. Conclusions

A detailed model of a fixed bed of these capsules with an embedded heat exchanger is presented in this chapter and used to simulate absorption-desorption cycles. The sensitivity of the fixed bed

with respect to flue gas residence time and absorber initial bed temperature is analyzed. One key observation is that the number of beds required is large, regardless of residence time. Thus, a carbon capture installation unit using fixed beds of MECS can be cumbersome in size if carbonate solution is the solvent. Obviously, the number of beds can be reduced by increasing the bed diameter. But beds of very large diameter can lead to issues related to non-uniform gas distribution. Therefore, experimental studies are needed to determine the largest practical diameter of the bed. The results of this study also demonstrate that heat recovery is necessary to keep the energy penalty of this system low. However, heat recovery could prove challenging in a real fixed bed system due to the gradients and transient temperature profiles in these beds. The modeling results also show that there's an optimum flue gas residence time to keep the number of beds at a minimum. The minimum number of beds required is around 90, each bed with a volume of 1767 m^3 , for a flue gas residence time of 100 s. A techno-economic analysis is performed where the equivalent annual operating cost (EAOC) is calculated for two different materials of construction- concrete, and carbon steel. The optimum EAOC depends on the material of construction, initial bed temperature, extent of heat recovery and residence time. With 85% heat recovery and a concrete contactor, the minimum EAOC is approximately 1.8 times higher than the EAOC of a conventional MEA absorber. The fixed bed techno-economic analysis indicates that the EAOC of MECS process using sodium carbonate solvent depends on combination of factors that are needed to reduce the economics. These factors include the absorber operating temperature, type of reactor construction material, residence time of flue gas, and heat recovery percentage.

When uncertainty is factored into the TEA, the minimum EAOC is still 1.5 times higher than the EAOC for a MEA absorber. The system size and cost results of this study demonstrate that a fixed bed configuration of capsules filled with carbonate solution isn't competitive with a conventional MEA absorber for carbon capture from a power plant. However, this modeling study is based on a very slow-acting core solvent (20wt% sodium carbonate solution) and serves as a starting point for MECS based CO_2 capture. Changing the core solvent in the capsules (e.g., using a higher carbonate concentration, an ionic liquid), would likely result in more competitive system sizes and costs. The model developed here provides a useful tool for modeling the performance and cost of fixed bed temperature swing absorption systems for encapsulated solvents.

Chapter 4. Moving Bed Modeling of MECS

The previous chapter focused on evaluating MECS technology in a fixed bed configuration. Another reactor configuration that is of interest for operating solid particles is moving bed reactor. This chapter introduces moving bed operation for MECS system where both absorber and regenerator process are simulated.

4.1. Introduction

The reactor level studies on MECS reported in the literature so far are mainly related to fixed bed or fluidized bed configurations. However, the moving bed setup for MECS has not been reported in the literature. As pointed in our earlier work [41], the fixed bed operation of MECS can lead to large number of parallel beds along with the associated difficulty in heat recovery, which is one of the critical aspects for reducing the energy penalty of CO₂ capture. Moving beds can offer near counter current interaction between the capsules and the gas thus improving the mass transfer driving force along the bed compared to the fluidized beds where the driving force can get significantly reduced due to the high mixing of solids and gases. Furthermore, moving beds also provide effective heat recovery option which is very difficult to achieve in fixed beds. Moreover, as separate beds are used for absorption and stripping in moving bed systems, these beds can be independently designed as opposed to the fixed beds where the same bed undergoes cycling operation between absorption and desorption. In addition, as the loading front moves with time in fixed beds, the contact time of the gas with unloaded or partially loaded solvent keeps reducing with time for a given bed during absorption thus a portion of the bed remain underutilized. In our earlier study, it was observed that the average bed loading was around 50% of the maximum loading that can be achieved if the entire bed could reach the equilibrium [41]. The underused portion of the beds impact the economics through increase in capital and operating costs of the process. Moving beds can help to achieve high solvent loading and allows considerably higher gas velocity compared to the fixed beds thus reducing the number of beds and improving utilization of the bed. Therefore, the process economics of moving bed operation will be inexpensive when compared to fixed bed.

The moving bed technology has been applied to several processes such as chemical looping combustion, fluid catalytic cracking, and pyrolysis [42]. The need for improving the commercial

feasibility of available carbon capture processes has led to more research for innovative configurations in the recent years [43-45]. The application of moving bed reactor for CO₂ capture in which attrition can be minimized by introducing perforated plates is shown to be a promising technology [46]. Luo et al. [47] demonstrated the viability of moving bed operation in coal direct chemical looping. Ku et al. [48] performed experimental studies on methane combustion using a lab-scale moving bed reactor. Studies on process modeling of the moving bed reactors for carbon capture are few [43,44,49,50]. A review of the literature on process modeling of the moving bed reactors for CO₂ capture can be found in the work of Bhattacharyya and Miller [51]. Kim et al. [43] proposed a simulated moving bed process with heat integration for CO₂ capture using Zeolite 13X. Kim et al. [49] developed a moving absorber bed model with embedded heat exchanger and applied to sorbent-based carbon capture. In the moving bed studies performed by Kim et al. [49] the heat transfer coefficient between the embedded heat exchanger and bed is inspired by the heat transfer correlations of a fluidized bed. Such correlations can overestimate the heat transfer coefficient, which in turn not only affect heat transfer, but also mass transfer, hydrodynamics, and economics of the process. A new correlation for heat transfer coefficient that takes into account the surface contact resistance and bulk penetration resistance is used in this study. Okumura et al. [52] demonstrated pilot level tests of CO₂ capture with a capacity of 1.6 tons per day where waste heat is used to reduce the energy requirements of the process. Yang et al. [53] performed a design study on reactor configurations where fluidized bed and moving bed are used for absorption and regeneration stages respectively. To the best of our knowledge, there is currently no process model in the open literature on the moving bed technology for CO₂ capture using MECS.

The economic studies on the moving bed processes for CO₂ capture are limited in the literature. Kim et al. [54] presented a comparison of bubbling fluidized, fast fluidized, and moving beds for CO₂ capture process retrofitted to 500 MW coal power plant using polyethylenimine (PEI) sorbent. The economics shown in their work conclude both moving and fluidized bed processes are lower than the conventional amine-based process and moving bed configuration is found to be slightly superior. Krutka et al. [55] provided a discussion on the capital cost of moving bed for CO₂ capture based on the information obtained from equipment vendors and mentions that cost is greatly impacted by the heat transfer area requirements. Jung et al. [45] focused only on the operating cost of simulated moving bed (SMB) process using amine functionalized solid sorbent. Miller et al.

[56] discusses a superstructure-based optimization for optimal selection of reactor type and operating conditions of CO₂ capture process using solid sorbents. A good review of post combustion carbon capture technologies focusing on capital cost, operating cost, and operability of solvent and sorbent systems can be found in Bhattacharyya and Miller [51]. A techno-economic optimization of a moving bed process is not reported in the literature for any CO₂ capture system.

The process modeling and economic evaluation of MECS technology in a moving bed configuration is not well studied in the literature. The present work contributes by developing a rigorous multiscale moving bed process model for MECS with sodium carbonate as the capture solvent. A techno-economic analysis including both capital and operating costs of the moving bed process is also presented. Further, an optimization study based on equivalent annual operating cost of the process is carried out in Aspen Custom Modeler.

4.2. Moving Bed Configuration and Modeling

Figure 4.1 shows the schematic of moving bed setup considered in the process modeling study. Unlike fixed bed configuration where the solids are stationary, solids flow down the bed and moves between the absorption and desorption stages. During absorption, the lean microcapsules enter at the top of the reactor and flows through the bed before it exits from the bottom. The CO₂-rich flue gas enters at the bottom of the bed and exits from the top. The CO₂-rich capsules and the clear flue gas leave from the bottom and top of the absorber, respectively. The CO₂-rich capsules enter at the top of the desorber through a pre-heat exchanger that heats up the incoming solids by recovering heat from the outgoing solids from the desorber through a heat transfer fluid. The energy required for regeneration is mainly provided by the condensation of the indirect steam in the embedded heat exchanger. Steam is also directly injected into the bed, which mainly helps to reduce the partial pressure of CO₂ while it may provide a small portion of the heat due to condensation depending on the operating conditions. The released CO₂ along with steam exits from the top of the bed while the lean microcapsules leave from the bottom of the bed. Lean microcapsules exchanges heat with the heat transfer fluid in a heat recovery exchanger and then cooled in a cooler using cooling water before being returned to the absorber.

Figure 4.1 Schematic of MECS moving bed configuration showing absorber and regeneration process.

The resulting near-countercurrent contact between the microcapsules and gas/steam leads to high driving force in the moving beds. Another advantage of using the moving bed compared to the fixed beds is the efficient recovery of the sensible heat from the hot lean microcapsules [57].

A first-principles mathematical model describing the moving bed absorber and regenerator stages is developed. The 1-D mathematical model is developed by considering the mass, energy, and momentum balance between gas, capsules, and heat exchanger tubes. The major assumptions considered in the development of the moving bed reactor model are outlined as follows:

- Thermal conduction along the axial direction is negligible compared to the convective transport.
- Voidage in the bed is uniform.
- Solvent does not permeate through the shell material. This is based on the experimental observation of the particular shell material and solvent.

Gas phase Species Conservation:

Mass balance of individual components in the gas phase is given by:

$$\varepsilon_b \frac{\partial C_{i,G}}{\partial t} = \varepsilon_b D_z \frac{\partial^2 C_{i,G}}{\partial z^2} - \frac{\partial(u_g C_{i,G})}{\partial z} - (1 - \varepsilon_b) a_{e, \text{cap}} N_{\text{surf}, G} \quad (4.1)$$

where i corresponds to species H_2O , CO_2 , N_2 .

Species conservation for the microcapsule:

The component mass balance for the species diffusing through the shell is given by:

$$\begin{aligned} (1 - \varepsilon_b) v_{f, \text{shell}} \frac{\partial C_{i, \text{shell}}}{\partial t} \\ = u_{\text{cap}} v_{f, \text{shell}} \frac{\partial C_{i, \text{shell}}}{\partial z} + (1 - \varepsilon_b) a_{e, \text{cap}} N_{i, G} - (1 - \varepsilon_b) v_{f, \text{core}} a_{e, \text{core}} N_{i, \text{shell}} \end{aligned} \quad (4.2)$$

where i corresponds to H_2O and CO_2 .

The mass balance for the components of the core fluid inside the microcapsule is represented as

$$u_{\text{cap}} \frac{\partial(C_{i, \text{core}})}{\partial z} + (1 - \varepsilon_b) a_{e, \text{core}} N_{i, L} = 0 \quad (4.3)$$

$$N_{i, G} = k_{i, G} (C_{i, G, \text{bulk}} - C_{i, \text{shell}}) \quad (4.4)$$

$$N_{i, \text{shell}} = k_{i, \text{shell}} (C_{i, \text{shell}} - C_{i, \text{int}}) \quad (4.5)$$

$$N_{i, L} = E k_{i, L} C_{\text{tot}, L} (x_{i, \text{int}} - x_i^*) \quad (4.6)$$

$$k_{i, \text{shell}} = \frac{D_{i, \text{shell}}}{W_{\text{thk}, \text{shell}}} \quad (4.7)$$

$$N_{i, \text{shell}} = N_{i, L} \quad (4.8)$$

where i corresponds to H_2O and CO_2 .

The total concentration of core liquid is given as

$$C_{\text{tot}, L} = \sum C_{i, \text{core}} \quad (4.9)$$

where i corresponds to H_2O , CO_2 , and Na_2CO_3 .

The vapor-liquid equilibrium for CO_2 and H_2O is given by:

$$\phi_{\text{CO}_2} P y_{\text{CO}_2, \text{int}} = H e_{\text{CO}_2} \gamma_{\text{CO}_2} x_{\text{CO}_2, \text{int}} \quad (4.10)$$

$$\phi_{\text{H}_2\text{O}} P y_{\text{H}_2\text{O}, \text{int}} = x_{\text{H}_2\text{O}, \text{int}} \gamma_{\text{H}_2\text{O}} f_{\text{H}_2\text{O}}^L \quad (4.11)$$

The enhancement factor is given as

$$E = Ha = \frac{\sqrt{k_1 C_{\text{OH}^-} D_{\text{CO}_2, L}}}{k_{\text{CO}_2, L}} \quad (4.12)$$

Energy balance Gas Phase

$$\begin{aligned} \varepsilon_b \frac{\partial(C_{T,g}H_g)}{\partial t} = & -\frac{\partial(u_g C_{T,g}H_g)}{\partial z} - (1 - \varepsilon_b)a_{e,cap}(N_{CO_2,G}\bar{H}_{CO_2,v} + N_{H_2O,G}\bar{H}_{H_2O,v}) \\ & - (1 - \varepsilon_b)a_{e,cap}h_{gs}(T_g - T_s) \end{aligned} \quad (4.13)$$

Energy balance Microcapsule

$$\begin{aligned} v_{f,shell}(1 - \varepsilon_b)\rho_{shell} \frac{\partial H_s}{\partial t} \\ = v_{f,shell}u_{cap} \frac{\partial(\rho_{shell}H_s)}{\partial z} - v_{f,core}(1 - \varepsilon_b)a_{e,core}h_c(T_s - T_c) \\ - (1 - \varepsilon_b)a_{e,cap}h_{gs}(T_s - T_g) - N_{hxt}a_{e,hx}h_{hxws}(T_s - T_{hxw}) \end{aligned} \quad (4.14)$$

$$\begin{aligned} (1 - \varepsilon_b) \frac{\partial(C_{T,L}H_c)}{\partial t} \\ = u_{cap} \frac{\partial(C_{T,L}H_c)}{\partial z} + (1 - \varepsilon_b)h_c a_{e,core}(T_s - T_c) + (1 - \varepsilon_b)a_{e,core}N_{CO_2,L}\bar{H}_{CO_2,L} \\ + (1 - \varepsilon_b)a_{e,core}N_{H_2O,L}\Delta H_{vap} \end{aligned} \quad (4.15)$$

Energy balance between bed and heat exchanger tube

$$N_{hxt}\pi d_t h_{hxws}(T_{hxw} - T_s) + N_{hxt}\pi(d_t - 2thx_w) h_{hxwt}(T_{hxw} - T_{tube}) = 0 \quad (4.16)$$

The pressure drop in moving beds is obtained by considering the relative velocity between the capsules and gas phase [58]. The superficial velocity in the Ergun equation is replaced with slip velocity and the modified Ergun equation to describe the pressure gradient in the axial direction of moving bed is given as

$$\frac{\partial P}{\partial z} = - \left\{ \frac{150\mu_g(1 - \varepsilon_b)^2}{(d_p\psi)^2 \varepsilon_b^3} \varepsilon_b \left(\frac{u_g}{\varepsilon_b} + \frac{u_{cap}}{1 - \varepsilon_b} \right) + \frac{1.75\rho_g(1 - \varepsilon_b)}{(d_p\psi)\varepsilon_b^3} \varepsilon_b^2 \left(\frac{u_g}{\varepsilon_b} + \frac{u_{cap}}{1 - \varepsilon_b} \right)^2 \right\} \quad (4.17)$$

One of the few constraints in designing the moving bed reactor is to keep operating below the fluidization regime so that capsules does not flow upwards. In order to maintain the moving bed regime in the reactor, the gas velocity in the bed should be less than minimum fluidization velocity, u_{mf} , given as [59]

$$\frac{1.75}{\psi \varepsilon_{mf}^3} \left(\frac{d_p u_{mf} \rho_g}{\mu_g} \right)^2 + \frac{150(1 - \varepsilon_{mf})}{\psi^2 \varepsilon_{mf}^3} \left(\frac{d_p u_{mf} \rho_g}{\mu_g} \right) = \frac{d_p^3 \rho_g (\rho_s - \rho_g) g}{\mu_g^2} \quad (4.18)$$

For all the simulation studies presented here, the following constraint is fulfilled along the length of the bed.

$$u_g < u_{mf} \quad (4.19)$$

The mass and heat transfer coefficients between gas and solid is obtained using correlation given below

$$Sh = \frac{k_g d_p}{D_g} = 2 + 1.1 Re_p^{0.6} Sc^{0.3} \quad (4.20)$$

$$Nu_p = \frac{h_{gs} d_p}{k_g} = 2 + 1.1 Re_p^{0.6} Pr^{0.3} \quad (4.21)$$

In the moving bed studies performed by Kim et al. [49] the heat transfer coefficient between the embedded heat exchanger and bed is inspired by the heat transfer correlations of a fluidized bed. The correlation is based on the fluidization number which accounts for the time fraction of gas bubbles coming in contact with the particles. This approach of characterizing the heat transfer coefficient by treating the gas phase as dispersed is specific to fluidized bed configurations. Such correlations may overestimate the heat transfer coefficient thus affecting heat and mass transfer, hydrodynamics, and consequently economics of the process. Moreover, that correlation does not take into account the immersed body heat transfer rather the heat transfer between gas and solid phases. In this paper, the heat transfer mechanism between the wall of the embedded heat exchanger and the microcapsules is motivated from Schlunder [60]. Schlunder [60] suggested a lumped parameter approach by combining the contact and penetration resistances to calculate the overall heat transfer coefficient. The overall heat transfer coefficient is given by:

$$\frac{1}{h_{xws}} = \frac{1}{h_{ws}} + \frac{1}{h_{sb}} \quad (4.22)$$

The contact resistance between the wall and the particle is due to the gas present in between them. The heat transfer coefficient between wall and immediate solid layer can be modeled by the correlation:

$$h_{ws} = \phi_{pf} h_{wp} + (1 - \phi_{pf}) \frac{\frac{2k_g}{d_{cap}}}{\sqrt{2} + \frac{2(l + \delta)}{d_{cap}}} \quad (4.23)$$

, where h_{wp} is the heat transfer coefficient for a single particle/capsule which is defined as

$$h_{wp} = \frac{4k_g}{d_{cap}} \left(\left(1 + \frac{2(l + \delta)}{d_{cap}} \right) \ln \left(1 + \frac{d_{cap}}{2(l + \delta)} \right) - 1 \right) \quad (4.24)$$

In Eq. (24), k_g is the thermal conductivity of the gas phase. ϕ_{pf} is plate surface coverage factor (usually a value of 0.8 is considered). δ is the roughness of the particle surface and l is the modified mean free path of the gas molecules given by

$$l = 2\Lambda \frac{(2 - Y)}{Y} \quad (4.25)$$

The mean free path Λ is given below and Y is the accommodation coefficient typically ranges between 0.8-1.

$$\Lambda = \frac{16}{5} \sqrt{\frac{RT}{2\pi M}} \frac{\eta}{p} \quad (4.26)$$

The time averaged penetration heat transfer coefficient from the bed surface adjacent to the wall to bulk is calculated by:

$$h_{sb} = \frac{2}{\sqrt{\pi}} \frac{\sqrt{(\rho c_p k_{eff})_{bed}}}{\sqrt{t}} \quad (4.27)$$

The contact time t is defined as the total residence time of the particles on the heat exchanger surface wall and is given by

$$t = \frac{L}{u_{cap}} \quad (4.28)$$

where L is the length of the heat exchanger wall.

The interaction between gas and the microcapsule is crucial in the analysis of reactor scale studies. The moving bed model described above uses a rigorous capsule model in describing the heat and mass transfer of the system. The capsule model is developed by considering the appropriate thermodynamics, kinetics, and physical properties of the solvent of interest. A detailed capsule level model along with validation using experimental data can be found in our earlier work [41]. The encapsulated liquid considered in this study is sodium carbonate solvent. The underlying thermodynamics, kinetics, chemistry, and heat of reaction for the sodium carbonate solution is reported in our work [41].

4.3. Moving Bed Results

The above mathematical equations describing the gas-capsule interaction in a moving bed setup is developed using Aspen Custom Modeler® (ACM). The equation-oriented model is capable of simulating both absorber and regenerator stages. The flue gas conditions used in the simulation studies are obtained from NETL baseline report for a 644 MWe gross subcritical pulverized coal power plant [34]. The flue gas has composition of 13 mol% CO₂, 15 mol% H₂O, and 72 mol% N₂. The flue gas at the inlet of the absorber is assumed to be saturated with water since the flue gas typically passes through a scrubber before the capture system. The dimensions of the absorber, regenerator, and heat exchanger tubes are provided in Table 4.1. The effect of important operating variables such as the lean capsule CO₂ loading, the lean capsule temperature, and the regenerator pressure on the economics of moving bed process is studied. The gas flowrate in the absorber and regenerator is maintained so that the minimum fluidization velocity constraint (Eq. 4.19) can be satisfied. The capsules flow into the absorber bed is computed for 90% CO₂ capture. The CO₂ capture percentage can be defined as the amount of CO₂ captured from the flue gas entering the capture plant. The equation for CO₂ capture is as follows:

$$\text{Carbon Capture (\%)} = 1 - \frac{y_{CO_2,in,abs} F_{gas,in,abs}}{y_{CO_2,out,abs} F_{gas,out,abs}} \quad (4.29)$$

where $y_{CO_2,in,abs}$ and $y_{CO_2,out,abs}$ are the CO₂ mole fraction in the gas stream entering and exiting the absorber respectively and $F_{gas,in,abs}$ and $F_{gas,out,abs}$ are the molar flow rate of the flue gas and clean flue gas leaving the absorber, respectively.

Table 4.1 Key design and operating variables of moving bed setup.

Variable	Value	Units
Reactor Diameter	7.5	m
Reactor Height	20	m
Heat Exchange Tube Diameter	0.0381	m
Lean Capsule Temperature	60	°C
CO ₂ Capture	90	%
<i>Capsule characteristics</i>		
Capsule Radius	3e-4	m
Core Radius	2.63e-4	m
Solvent Concentration	20	wt%

4.3.1. *Effect of lean loading.* The impact of different lean loadings on key variables are presented here. From Fig. 4.2, as the lean loading is increased, the capsules flowrate required for 90% capture keeps increasing. As the capsules flowrate keeps increasing, its residence time in the bed decreases resulting in a decrease in the rich loading, that keeps moving further from the equilibrium loading, which in turn leads to higher capsules flow for 90% capture. This combined effect leads to steeper increase in the capsules flow and decrease in the rich loading with the increase in the lean loading.

Figure 4.2 Effect of lean loading on lean capsule flow and rich loading.

The effect of lean loading presented in Figure 4.2 depends on the absorber reactor length since that affect the residence time. Figure 4.3 shows the variation in the lean capsule flow with lean loading for different reactor lengths. For a higher lean loading, capsule circulation flow becomes very high when the reactor length is low. This can be seen for the case when the reactor length is 12.5 m and correspondingly the capsule flow is significantly higher. As the reactor length increases, the required increase in the capsule flow for an increase in the lean loading becomes much lower as the capsule residence time remains reasonably high for the capsule to reach close to the equilibrium loading. Obviously, the sensitivities presented in Figures 4.2 and 4.3 depend on the kinetics of the solvent at the reactor operating conditions. It can be noted that Na₂CO₃ has slower kinetics compared to many amine solvents such as MEA [36].

Figure 4.3 Effect of lean loading on capsule flow for different reactor lengths.

As mentioned earlier, one of the advantages of moving bed operation against a fixed bed is that the absorber and regenerator can be independently designed. The number of parallel beds in the absorption stage is obtained to meet the demand of continuous processing of the flue gas coming from the power plant. The total number of beds is calculated by adding number of parallel beds in the absorption and desorption. Figure 4.4 presents the sensitivity of lean loadings on the total number of beds. It can be noticed that there is an optimum number of beds with respect to the lean loading. As the lean loading increases, the capsule flow continues to increase to meet the set CO₂ capture percentage as observed in Figure 4.3. As the flow of lean capsules flow is increased, larger number of absorption beds are desired to maintain the bed profile before minimum fluidization velocity. As observed in Figure 4.3, there is steeper rise in lean capsule flow with beds of shorter length and therefore steeper rise in number of beds for beds of shorter length with the increase in the lean loading. In Figure 4.4, it can be observed that as the lean loading decreases further there is a steep rise in number of beds irrespective of the length of the bed. This is because of the steep increase in the number of beds undergoing regeneration at low lean loading. For achieving increasingly lower lean loading, considerably higher residence time is required thus requiring higher number of regenerator bed even with the decrease in the capsule circulation flow.

Figure 4.4 Effect of lean loading on total number of beds present in the moving bed setup.

One of the key variables in the analysis of CO₂ absorption is the regeneration duty. Figure 4.5 shows the sensitivity of regeneration energy with respect to lean loading. At higher lean loadings, the capsule circulation flow is higher which requires a larger amount of sensible heat for heating the capsules. Obviously, the required sensible heat becomes much steeper for the bed of lower lengths as the circulation rate becomes steeper for shorter beds as shown in Figure 4.3. For lower lean loading, while sensible heat requirement decreases due to lower circulation flowrate, the regeneration energy increases mainly due to higher amount of water vaporization. The study shows that there exists an optimal lean loading with respect to regeneration energy.

Figure 4.5 Effect of lean loading on the regeneration duty.

The studies presented above shows that the higher reactor length can have a number of advantages. However, the increase in length leads to an increase in the capital cost of a given bed. Furthermore, the design and operating constraints like pressure drop, and minimum fluidization velocity need to be considered to determine the dimensions of the reactor. Therefore, an optimization considering the economic and design constraints is required for optimizing the dimensions.

4.3.2. Effect of lean capsule temperature. One of the important operating conditions that has significant impact on the economics of CO₂ absorption is the lean capsule temperature. The variation in lean capsule temperature leads to changes in the amount of capsule loading and the capsule flowrate needed to achieve the desired CO₂ capture. Figure 4.6 presents impact of lean temperature on rich loading and capsule flowrate. At low temperatures, especially for carbonate solutions, the reaction rate becomes slower and therefore more capsules are needed for CO₂ absorption. As the lean capsule temperature is increased to about 60°C, more CO₂ gets absorbed into capsules thus increasing the rich capsule loading and decreasing the lean capsule flow. Further increase in the temperature leads to a detrimental effect due to adverse effect on vapor-liquid equilibrium leading to an increase in the capsule circulation flowrates at higher temperature as shown in Figure 4.6. It can be noted that these tradeoffs between kinetics and thermodynamics is considerably more pronounced for Na₂CO₃ compared to typical amine solvents like MEA.

Figure 4.6 Effect of lean capsule temperature on rich loading and lean capsule flow.

Figure 4.7 shows the sensitivity of lean loading on the number of beds needed for three different lean capsule temperatures entering the absorber. The volume of a single reactor for the dimensions reported in the Table 4.1 is 880 m³. At lower temperatures such as 40°C, more capsules are required to circulate in the bed to account for slower reaction rates leading to higher number of beds. At higher temperatures such as 80°C, total number of beds rises again due to the increase in the capsule flow as shown in Figure 4.6. At intermediate temperature such as 60°C, the total number of beds is lower compared to 40°C and 80°C irrespective of the lean loading. Irrespective of the inlet temperature, the number of beds steeply increases as the lean loading becomes very low due to the sharp increase in the number of regeneration beds similar to what has been observed in Figure 4.4.

Figure 4.7 Effect of lean loading on total number of beds present for different lean capsule temperatures.

4.3.3. Effect of heat transfer coefficient. The heat transfer coefficient between the immersed body and the bed is calculated with the correlation mentioned above and it is compared with the one in Kim et al. [49] that is based on drawing similarity with the fluidized beds. Due to the higher turbulence in fluidized beds compared to the moving beds, it is expected that correlations similar to fluidized beds can overpredict the heat transfer coefficient for moving beds. Figure 4.8 shows the heat transfer coefficient profile along the length of the bed calculated using both correlations. The heat transfer coefficient calculated with the correlation used in the study of Kim et al. [49] results in almost double the value obtained with the correlation used here. The heat transfer

coefficient can have a significant impact on the heat duties, mass transfer, and overall performance of the moving bed.

Figure 4.8 Comparison of heat transfer coefficient values along the bed length for the two different correlations.

The impact of heat transfer coefficient on the flow rate of H_2O in the gas phase is presented in Figure 4.9. The steam enters from the bottom ($z/L=0$) and exits ($z/L=1$) at the top of the desorber. The capsules enter from the top ($z/L=1$) and exits ($z/L=0$) at the bottom of the desorber. The molar flow of H_2O in the gas phase increases as the water gets vaporized from the capsules before it starts decreasing at the top of the bed. When the heat transfer coefficient is high, more water gets vaporized which increases the flow rate of H_2O as shown in Figure 4.9 as compared to lower heat transfer coefficient. This increase in water vaporization led by higher heat transfer coefficient (heat duties) can make the operating cost to go up. The study shows that the correlations for heat transfer coefficient in moving beds would strongly affect model results. Unfortunately, the current literature lacks experimental data on heat transfer characteristics for moving beds especially in presence of embedded heat exchangers.

Figure 4.9 Sensitivity due to heat transfer correlations on the gas phase water flow in the desorber.

4.4. Techno-Economic Analysis

The information about economics of novel technologies like MECS is not available in the open literature for any scale. The techno-economic analysis accounts for total capital and operating cost of the MECS moving bed system. The capital cost includes reactors, compressors, raw materials and operating cost includes the energy requirements for compressors, regeneration, and capsules transport. The cost for absorber and regenerator is calculated using Aspen Process Economic Analyzer (APEA). The reactor capital cost calculated includes equipment cost, material cost, labor cost (both direct and indirect) for installation including freight, overhead, engineering services. The equipment cost for balance of the plant such as compressors, heat exchangers are also included in the cost. The operating expenses includes the steam cost for the regeneration of CO₂, electricity cost for the compressors and bucket elevators. The cost of the low-pressure process steam is taken from Turton et al. [38] to calculate the operating cost. The cost of electricity is taken from U.S Energy and Information [61] is an average price of electricity for the use in industrial sector.

The absorber moving bed reactor does not have any embedded tubes and is represented as a vertical cylindrical vessel in the APEA to obtain the absorber cost. This representation of absorber in APEA might be underestimating the capital cost for process as there might be cost associated with bed internals. Therefore, an uncertainty analysis in the capital cost of the reactors is undertaken.

The regenerator reactor has an embedded tubular heater which is represented as shell and tube heat exchanger in APEA for the equipment cost. The cost of the capsules including the solvent and the polymer shell can be found in our earlier work [41]. The cost of compressor required to compress the flue gas to meet the absorber inlet pressure is calculated using APEA. The cost of the lean/rich capsule heat exchanger is calculated as a function of capsules cooling duty and cost based on kW of the duty (S) using Eq. (4.30). The value of cost per unit duty (S) is taken to be \$50/kW.

$$Cost_{CrossHX} = S Q_{CrossHX} \quad (4.30)$$

The cost for distributor is computed using Eq. (4.31) which is defined as a function of diameter of the bed is given as [62]

$$Cost_{distrib} = 125 \left(\frac{\pi}{4} \right) (3.281 D_b)^2 \quad (4.31)$$

The transportation of solids between absorber and regenerator is assumed to be taking place using bucket elevators. Bucket elevators are an efficient way of transporting solids in bulk materials handling industries due to their compact design for a wide variety of materials. The horsepower required to move the capsules between absorber and regenerator can be calculated as [63]

$$P_{BE} = Q(D_H + 10')(3.23e^{-5})(DSF) \quad (4.32)$$

where Q is the volumetric capacity of the elevator (bushels/hr), D_H is the discharge height and DSF is the drive safety factor applied to belt drives used in the elevator and it typically varies between 1.3-2.0 depending on the class of drives.

The equivalent annual operating cost (EAOC) is calculated to describe the economics involved in the MECS moving bed configuration. The EAOC value is summation of the annualized capital cost to the yearly operating cost (YOC) as presented in section 3.4. The annualized capital cost is computed by annualizing the total capital cost over the time of plant life. The discount rate is assumed to be 10% and the operating life for the reactors and compressors, is assumed to be 10 years and 2 years for the capsules. The TEA of the MECS system is compared with that of conventional MEA-based CO₂ capture in towers. For the MEA system, capital and operating costs are obtained from Case 11B in the National Energy Technology Laboratory (NETL) baseline study [34].

4.4.1. Optimization Setup. The optimization of MECS moving bed reactor is formulated with an economic objective function along with the set of decision variables. The objective function considered in this study is minimization of the equivalent annual operating cost (EAOC) that is defined in the earlier section. The decision variables include design and operating conditions of the process that can be varied to minimize the EAOC value. The optimization problem is formulated as:

$$\begin{aligned}
 \min f(x) &= EAOC \\
 \text{s.t. } h(x) &= 0 \\
 g(x) &\leq 0 \\
 x_L &\leq x \leq x_U
 \end{aligned} \tag{4.33}$$

In the above equation, the objective function $f(x)$ is the process economics described using EAOC; $h(x)$ and $g(x)$ are the equality and inequality constraints of the process model presented earlier in section 4.2. One of the flowsheet level constraints considered in the optimization is to ensure the reactor is maintained under minimum fluidization condition ($u_g < u_{mf}$). The moving bed absorber and regenerator is set to be operated at 85 % of minimum fluidization velocity. The other flow sheet level constraint is the pressure drop in the reactors which is posed as a nonequality constraint. Another important equality constraint is the amount of CO₂ capture from the flue gas and its value is set to 90% in this study. These constraints are given below as

$$\begin{aligned}
 u_g &= 0.85u_{mf} \\
 0 &\leq \Delta P < 0.3 \\
 CO_2 \text{ Capture} &= 0.9
 \end{aligned} \tag{4.34}$$

One of the important variables to be considered in the scale up of any process is the reactor dimensions, height, and diameter. The design decision variables considered in the optimization are the lengths of both reactors. The ratio of bed height to diameter defined as aspect ratio is crucial in the distribution of the flue gas and pressure drop in the reactors. In deciding the aspect ratio of the reactor, two important factors that needs to be considered are the capital cost and reactant distribution inside the reactor. A lower L/D ratio can lead to uneven distribution of the stream entering the reactor. Aspect ratio is another design decision variable included in the optimization here. Other decision variables are the operating conditions of the process that impacts the performance of CO₂ capture. The operating variables of interest in this study are lean capsule

loading, lean capsule temperature, and indirect steam flow. The decision variables included in the optimization studies along with their lower and upper bounds are presented in Table 4.2.

Table 4.2 Moving Bed Optimization Results

Decision variables	Initial value	Result	Lower bound	Upper bound	Units
Design:					
Absorber bed height, (m)	11	16.9	8	18	m
$\left(\frac{L}{D}\right)_{abs}$	3.5	2.3	2	5	-
Regenerator bed height	10	12.1	8	18	m
$\left(\frac{L}{D}\right)_{reg}$	3.5	3	2	5	-
Operating:					
Lean loading	0.11	0.13	0.1	0.165	molHCO ₃ ⁻ /molNa ⁺
Lean capsule temperature	60	67	40	80	°C
Indirect Steam flow	385	415	100	1000	kmol/hr

The above-described formulation is setup in Aspen Custom Modeler® to perform steady state optimization using inbuilt optimization solver. For every iteration the moving bed model is simulated with the decision variables given by the solver and the EAOE is calculated. The objective function calculating the EAOE value is defined in the flowsheet section and the decision variables are exposed to the optimization solver. The capital cost and operating cost calculations resulting the EAOE of the process is defined in the flowsheet section. The optimization proceeds until there is no reduction in the EAOE value up on varying the decision variables. The optimization problem is solved using Nelder-Mead algorithm and the results are presented in Table 4.2.

The equivalent annual operating cost (EAOE) for MECS moving bed system obtained using the solution in Table 4.2 is shown in Figure 4.10. The EAOE value for MEA system taken from NETL

baseline study [34] is also plotted in Figure 4.10. It can be seen from the figure that EAO value is much higher than MEA system and this is due to zero heat recovery from the sensible heat of the capsules leaving the regenerator. Heat recovery plays a crucial role in reducing the heat requirements in the desorption of CO₂. The heat recovery section can be designed for different extent of heat recovery. In this study, the impact of heat recovery is evaluated for two different recovery percentages and their EAO value are shown in the Figure 4.10. For sensible heat recovery of 85%, which is similar to MEA systems, the EAO value is found to be lesser than conventional MEA system.

Figure 4.10 Impact of heat recovery on EAO values for MECS moving bed setup and their comparison with conventional MEA process.

The capital cost of moving bed reactor is not well established in the open literature as the fabrication requirements are based on the process of interest. For novel technologies like MECS it is further difficult to estimate the capital cost as there is no previous data or information either on a pilot or industrial scale in the open literature. Even though the capital cost for the reactors is obtained using APEA, there can be still uncertainty as the moving bed reactors are for solids can be customized to process requirements. Therefore, an uncertainty of $\pm 50\%$ is considered in the capital cost for 85% heat recovery and the results are shown in the Figure 4.11. An uncertainty of +50% in the capital cost makes the EAO value greater than MEA system showing the impact of heat recovery and capital cost.

Figure 4.11 Effect of capital cost uncertainty on the EAOC values of the MECS moving bed configuration.

4.4.2. Impact of part load operation. Power plants frequently vary their load throughout the day to change in the electricity demand and supply, more so with the increased penetration of renewables into the grid. Traditional design of capture systems is done to achieve the CO₂ removal target from the flue gas coming from power plants operating under full load conditions. However flexible CO₂ capture accounting the flue gas conditions variability due to part load operation of power plant can provide operational cost savings. Therefore, it is imperative to understand the performance of CO₂ capture system under part load scenarios. One of the important variables that can provide this measure is annualized operating cost. The operating economics of the CO₂ capture system significantly depends on the incoming flue gas from the power plants that are subjected to fluctuating loads. This sensitivity can be captured through operating cost variation with part load as shown in the Figure 4.12. Figure 4.12 shows the simulation results for the optimum capsule flow necessary for 90% capture at three different plant loads 70%, 85% and 100%. The capsule flow decreases with decrease in the plant load as the total amount of CO₂ capture goes down. This decreasing capsule flow leads to a reduction in the operating cost of the capture system.

Figure 4.12 MECS operating cost sensitivity with part load of the power plant.

4.5. Conclusions

A detailed 1-D non-isothermal moving bed model is presented for the micro encapsulated carbon sorbent (MECS) technology with sodium bicarbonate as the encapsulated solvent. An embedded heat exchanger in the regenerator along with direct steam injection is used to provide the required regeneration energy of the capture system. The impact of design and operating variables on the performance of MECS moving bed configuration is presented. Mainly, the sensitivity of capsule lean loading, dimensions of the reactor, and lean capsule temperature on the economics of the capture system is studied. The sensitivity results show that higher reactor lengths lead to reduction in the total number of beds required to process the flue gas. The modeling results also show that there is an optimum lean loading at which the capture system can be economically operated. The moving bed reactor optimization considering the design and operating variables subjected to the constraints is conducted. The optimization study seeks to minimize the EAO of the moving bed reactor and the results show that the performance of MECS system is 8% better compared to traditional MEA system at a similar heat recovery. An uncertainty analysis on capital cost is presented and the results show that at MECS system is better compared to the MEA for an uncertainty of -50%. The EAO of the MECS system is competitive to MEA at higher heat recovery percentages. The sensitivity of the MECS capture system at part load conditions of the power plant is also studied.

Chapter 5. Soft Sensor Development and Control Studies on Moving Bed Process using MECS

The previous chapter presented the modeling approach and techno-economic optimization of moving bed reactor using MECS for CO₂ capture. It is crucial to understand the operational difficulties that can occur when technologies are scaled up to meet the industrial needs. In the case of CO₂ capture technologies, the CO₂ capture process is tightly integrated to another different process that has many dynamic components involved in its daily operation, here it is power plants producing electricity using coal or natural gas. The understanding of how to effectively operate the MECS based capture process is of utmost interest as the encapsulation of solvent brings the uncertainty in the solvent state.

5.1. Introduction

The dynamic analysis of CO₂ capture in a moving bed process is rare as most of the related studies focused on reactor development and steady state operation [44,45,55]. Kim et al. [49] presented the dynamics of a standalone moving bed regenerator model for CO₂ capture using a polyethyleneimine sorbent. The understanding of dynamic operation of CO₂ capture process is crucial in evaluating various technologies. This is also important in view of flexible carbon capture and storage initiative by U.S DOE to help power producers to respond to grid fluctuations and penetration of renewable energy. The load variations in power plant requires the capture plant to respond dynamically that can help to produce electricity in an economically viable manner. Bhattacharyya and Miller [51] describes the importance of dynamic operation and control especially for the combination of solid sorbents with various reactor configurations. The review [51] points out the lack of solid sorbent dynamic studies and how such analysis can be helpful to understand the response of capture system when it is integrated to the power plant. The integration of capture unit to the power plant requires an advanced control framework not only to dynamically move from one operating condition to another, but also respond to the input disturbances resulting from load fluctuations. Recently Yu et al. [64] implemented an economic-NMPC for the CO₂ capture system in a bubbling fluidized bed and compared its performance against the setpoint tracking formulation. Kim et al. [49] implemented a LMPC on the regenerator section alone and did not consider the dynamics of a capture system where both absorber and desorber are connected. The control objective in their study is to maintain the regeneration capacity of the bed where solids

loading from the model is directly used in the objective function, a variable that cannot be measured. The study only considers the steam flow to the internal heat exchangers as the manipulated variable to meet the control performance even though both direct and indirect heating medium were used. In the present work, the capture unit using MECS technology with both absorber and regenerator models is used to implement the LMPC to control key process variables. From an operating standpoint, the capture percentage and desorber exit temperature are generally identified as important control variables [65,66].

It is of great interest to have information on key process variables to produce a reliable performance from any process. This information is mainly obtained by installing measuring devices at the required locations in the processes. However, measuring some variables can be challenging due to hostile environment for the device, infrequent sampling ensuing from an offline analysis in a laboratory, or difficulty in the sample collection, to name a few. Mathematical models can play a huge role to provide cost-effective solutions to overcome these practical limitations. In the case of MECS, the solvent is encapsulated inside a microcapsule, and it is a challenge to know the solvent concentration and provide makeup as done for the traditional solvent systems. While it is difficult to measure the solvent concentration present inside the microcapsule, it is important to know the capsule water content to obtain the desired operating performance of the MECS system. The models developed to estimate such process variables can be referred as inferential models, virtual sensors, or soft sensors [67]. Soft sensors help to infer the values or information of unmeasurable or difficult to measure variables by using the data of the easy to measure variables. The underlying mathematical models for the soft sensor are based on mechanistic, data-driven, or hybrid approaches. The data driven approach is an empirical relationship between outputs and inputs and does not require the inherent knowledge about the process instead completely depends on the quality of the data used for estimation. These empirical data driven models describing the input-output relation can be linear or nonlinear based on the complexity of the data.

MECS can gain or lose water depending on the operating conditions thus leading to variation in concentration over time. In practical operation, if the solvent concentration cannot be maintained, it can lead to serious loss of performance over time. However, the inability to measure the capsule solvent concentration makes it more interesting and challenging to maintain the water content along with the other key process variables at their desired setpoints. Here we propose to measure and control surrogate variable(s) that can ensure desired concentration of the solvent. These

variables will be used for a model-based estimation ('soft sensing') of water concentration in the solvent. The phase equilibrium relates the gas phase water composition to the capsule core concentration and therefore the partial pressure of water along with the temperature can be used as main surrogate variables. However, the counter current configuration and the kinetic limitations limits the possibility of capsules to reach the equilibrium while exiting the bed. The partial pressure and temperature measurements at different locations in the bed can serve as candidate surrogate variables. Hence, it becomes imperative to identify the most sensitive set of surrogate variables that can relate to the exit core concentration.

The contributions in this chapter can be summarized as, (1) The moving bed capture unit with both absorber and desorber is used for control studies. (2) A linear model predictive controller is used to control the key operating variables in MECS system. (3) A soft sensing approach is proposed to estimate the state of microcapsule water content and the developed soft sensor is then integrated into a control framework to help operate the moving bed process.

5.2. Soft Sensor Development

In this study, the water content in the capsule leaving the reactor is inferred in an economic and reliable way with the help of reactor temperature, partial pressure of H₂O, and CO₂ capture measurements. The soft sensor for capsule water content exiting the reactor is developed for both the absorber and desorber. The difficult (impractical) to measure water content is termed as primary variable and easy to measure temperature, partial pressure, capture percentage are referred as secondary variables.

An input-output model relating primary variable (y), and the secondary variable (x) obtained from the rigorous process model is developed. The model structure along with the selection of input variables that are used in it plays a crucial role in the performance of soft sensor and computational framework where it is resided. There are numerous soft sensor approaches reported in the literature based on the application and structure of the mathematical model [68-74]. In general, the soft sensor model can be mathematically represented as

$$y = f(x_1, x_2, x_3, \dots, x_n) \quad (5.1)$$

The function f can be linear or nonlinear. Capsule water content leaving the reactor can be seen as the output y in the above formulation. One of the important challenges in developing the soft sensor model is the selection of secondary variables that are included as inputs (x) in the soft sensor modeling framework. The candidate inputs for the soft sensor must be measurable, their measurement should be available at least at the frequency at which it is desired to estimate the primary variable, and the measurements should be cost-effective. The candidate inputs can include both measured manipulated/disturbance inputs and outputs. For this system, the candidate inputs are capsule flow, direct steam flow, indirect steam pressure, flue gas flow, CO₂ capture, temperature, and partial pressure of H₂O in the absorber and desorber at different locations. The axial variation in the variables is assumed to be available at every 1.7 m and 1.2 m for absorber and desorber reactors respectively. This results in 10 candidate measurements of pressure and temperature sensors each in absorber and a similar number in desorber. Therefore, the total number of candidate sensors that can be used as inputs to the soft sensor amounts to 45 (5+ 2*10 +2*10). In the literature, various approaches have been studied in relation to secondary variables selection criteria while developing a soft sensor model [67,71,74]. In this work, the appropriate variables are selected based on the correlation and principal component analysis. The gain matrix at every time instant comprising the approximation of derivatives of each secondary variable with respect to the primary variable is defined as

$$G(t) = \begin{bmatrix} \frac{\Delta x_1}{\Delta y_1} & \dots & \frac{\Delta x_1}{\Delta y_i} & \dots & \frac{\Delta x_1}{\Delta y_k} \\ \vdots & \dots & \vdots & \dots & \vdots \\ \frac{\Delta x_j}{\Delta y_1} & \dots & \frac{\Delta x_j}{\Delta y_i} & \dots & \frac{\Delta x_j}{\Delta y_k} \\ \vdots & \dots & \vdots & \dots & \vdots \\ \frac{\Delta x_n}{\Delta y_1} & \dots & \frac{\Delta x_n}{\Delta y_i} & \dots & \frac{\Delta x_n}{\Delta y_k} \end{bmatrix}^T \quad (5.2)$$

where n is the number of secondary variables and k is the number of primary variables [71]. The principal components analysis (PCA) is then applied on $G(t)$, obtained using normalized variables, to identify the most sensitive secondary variables with respect to the primary variable [75,76]. The PCA can be used to decompose $G(t)$ into two matrices whose linear combination corresponds to maximum variance.

$$G(t) = UZ^T \quad (5.3)$$

where U is referred as the score matrix and Z as the loading matrix. The matrix Z provides the measure related to the secondary variables where the highest to lowest loading values corresponds

to most sensitive variable to least sensitive variables. The variables with highest loading values when included as inputs will help in estimating the primary variables more accurately. A correlation analysis is done between the secondary variables obtained from the PCA approach to further reduce the set of secondary variables. The final set of inputs for the soft sensor model of both absorber and desorber is shown in Table 5.1. The subscript x in temperature and pressure variables provided in the table 5.1 corresponds to normalized spatial location of the measurement from the bottom of the reactor. For e.g., the variable $P_{H_2O,x=0.5}$ represents the partial pressure of H_2O at half the length starting from the bottom of the reactor.

Table 5.1 Variables used as inputs to the soft sensor model.

Core H ₂ O Soft Sensor	Inputs	
	PCA	PCA + Correlation Analysis
Absorber	CO_2 capture %, $P_{H_2O,x=0.4}$, $P_{H_2O,x=0.5}$, $P_{H_2O,x=0.6}$ $T_{g,x=1}$, <i>Flue gas flow, Capsule flow</i>	CO_2 capture %, $P_{H_2O,x=0.5}$, $T_{g,x=1}$, <i>Flue gas flow, Capsule flow</i>
Desorber	CO_2 capture %, $T_{g,x=0.6}$, $T_{g,x=0.7}$, $T_{g,x=0.8}$, <i>Flue gas flow, Capsule flow,</i> <i>Direct steam flow, Indirect steam pressure</i>	CO_2 capture %, $T_{g,x=0.6}$, $T_{g,x=0.8}$, <i>Flue gas flow, Capsule flow,</i> <i>Direct steam flow, Indirect steam pressure</i>

System Identification: PRBS signal for surrogate models

The data for developing soft sensor requires persistent excitation of the process. Figure 5.1 presents the PRBS signal implemented on the rigorous model to obtain the input-output data needed for the soft sensor development. To be used in the model predictive control, a reduced model for the system should also be identified. The data for identifying the reduced model is generated by perturbing the inputs using the pseudo random binary signal (PRBS). PRBS is a two-level periodic, deterministic signal with covariance similar to the white noise. However, opposed to the flat power spectrum of white noise, the power spectrum of the PRBS signal is an impulse train. Therefore, the data for system identification can be generated by designing PRBS for all inputs ensuring persistence excitation of the process. A PRBS signal is characterized by two parameters, the duration of the switching sequence (N_s) and the switching time or clock period (T_{sw}) which is the minimum time between changes in the level of the signal. Rivera and Jun [77] have suggested guidelines for specifying T_{sw} and N_s as below

$$T_{sw} = \frac{2.78\tau_{dom}^L}{\alpha_s} \quad (5.4)$$

$$N_s = \frac{2\pi\beta_s\tau_{dom}^H}{T_{sw}} \quad (5.5)$$

where τ_{dom}^L and τ_{dom}^H are low and high values of the dominant time constant. β_s is a integer representing the settling time of the process (for 95% β_s is 3 and 99% β_s is 5) that determines the length of the test. Parameter α_s represents the expected closed-loop speed of response, typically set to a value of 2. A delay D between each input variables is required to avoid cross correlation between signals for a multivariate system. The delay is calculated as below [77]

$$D = \frac{T_{settle}}{T_{sw}} \quad (5.6)$$

The overall time needed to implement the signal for a given input is $t_f = T_{sw}N_s$. PRBS is designed for the 3 manipulated inputs-capsule flowrate, direct and indirect steam flowrates- and 1 disturbance input- flue gas flowrate- as shown in Figure 5.1. The key controlled variables of interest are the CO₂ capture percentage, desorber bottom temperature, and core solvent H₂O concentration at the exit of the bed.

Figure 5.1 PRBS generated values of inputs for system identification.

5.3. Controller Development

Figure 5.2 presents the control setup developed using MATLAB/Simulink and Aspen Custom Modeler. The CO₂ capture percentage, desorber bottom temperature are key variables for the performance of capture system [65]. As mentioned earlier, another important variable for MECS based capture system is minimizing the water loss or gain in the desorber from the capsules. The overall change in capsule water can be kept to minimum by making sure the capsule water content leaving the desorber is close to capsule water content entering the desorber (equal to the value leaving the absorber). Therefore, the controlled variables for this system are the capture percentage, desorber bottom temperature, and desorber exit capsule water content. The soft sensors are developed using the approach presented in the earlier section to provide the estimates of the capsule water content which are used as a measured value for the control framework shown in Figure 5.2. The output from desorber soft sensor representing capsule water concentration exiting the desorber acts as a controlled variable and the output from absorber soft sensor indicating the capsule water concentration entering into the desorber serves as its setpoint. This leads to a challenging control problem since the setpoint for the desorber exit capsule water content becomes time-varying. On the other hand, the setpoints for the capture percentage and desorber bottom temperature can be set at their desired values. The manipulated variables used are the capsule circulation flowrate, direct steam flow, and indirect steam pressure.

Figure 5.2 Control Architecture using soft sensor model.

Due to the strong interaction between the output variables, model predictive control (MPC) is a good candidate for controlling this system. The MPC is given by the following dynamic optimization problem:

$$\begin{aligned}
 \min J = & \sum_{i=1}^P (r_{k+i} - y_{k+i})^T w_y (r_{k+i} - y_{k+i}) + \sum_{j=0}^{M-1} \Delta u_{k+j}^T w_u \Delta u_{k+j} \\
 & y = f(u) \\
 & u_{min} \leq u_k \leq u_{max} \\
 & \Delta u_{min} \leq \Delta u_k \leq \Delta u_{max} \\
 & y_{min} \leq y_k \leq y_{max}
 \end{aligned} \tag{5.7}$$

The objective function J in the above MPC formulation is a quadratic cost function. In eq (5.7), r indicates the desired set point for the outputs, y refers to the model predicted outputs, and u denotes the manipulated variables or inputs used to control the outputs. P is the prediction horizon, M is the control horizon, and w_y and w_u are the output and input weighing matrices, respectively. The equality constraints ensues from the identified process model presented before. Bounds on inputs and outputs are also included in the above formulation. It can be noted that soft sensor is used as each execution step to compute the inlet and exit core H₂O concentrations. The linear model predictive controller is designed and implemented in MATLAB/Simulink and interfaced with the ACM model that serves as the true plant.

The MPC Designer toolbox available in the MATLAB is used for tuning the controller performance. The theory and implementation of MPC can be found in Morari et al. [78]. The MATLAB MPC toolbox user's guide documentation [79] is also helpful in navigating through the software. The linear state space model representing the nonlinear moving bed model acts as the plant for MPC. The sample time used in developing surrogate models is 5 seconds and it is also the control time step used in the MPC. The prediction horizon and control horizon values are manipulated to obtain the desired performance for MPC. The 'Aspen Model' in the Figure 5.2 is a user defined Simulink block based on S-Function. The parameters needed to input in the Simulink block are the ACM file name along with the model input and output variables that are needed for the control purpose. The 'soft sensor' blocks in the Figure 5.2 are identified linear models represented as 'Idmodel' block in Simulink. A variable step discrete solver is used in the Simulink to run the control setup presented above. The simulation is run from the Simulink so the communication time between Simulink and ACM is set by Simulink solver. At every time step,

the calculated values from MPC are passed onto the ACM to run the nonlinear and Simulink waits for the ACM to return the values of output variables. The ACM uses its own solver settings to run the nonlinear model.

5.4. Soft Sensor and Control Results

The analysis related to dynamic simulations can provide key insights into the transient behavior of the process that can be helpful in designing control systems. For CO₂ capture systems, key disturbance variables are flue gas flow, composition of CO₂ in the flue gas, and the key manipulated variables are the capsule flow, and direct and indirect steam flowrates. The moving bed model is used to study CO₂ capture dynamic response to the ramp changes in the flue gas flowrate, CO₂ composition in the flue gas, lean capsule flow rate, and direct steam flow rate. The base operating conditions for the dynamic studies shown in this section are obtained from the optimization results presented in the previous section. The dynamic response of CO₂ capture with respect to $\pm 5\%$ change in the flue gas flow and $\pm 5\%$ change lean capsule entering the absorber is presented in Figure 5.3. The nominal CO₂ capture used in the optimization to obtain the operating conditions is set to 90% which is also plotted in the figure as a reference. Disturbances in the flue gas flow and lean capsule flow were introduced as a ramp for moving bed setup including both absorber and regenerator. The decrease in flue gas flow increases the residence time of flue gas in the absorber which leads to an increase in the CO₂ capture percentage and vice versa. The CO₂ capture shows a maximum and minimum before settling down to a steady state value for the decrease and increase in the flue gas flow respectively. A similar response can be seen in the CO₂ capture due to change in lean capsule flow. As the capsules entering the absorber is decreased, the CO₂ capture goes down due to decrease in the capacity to absorb the CO₂ from the flue gas.

Figure 5.3 Dynamic response in CO₂ capture percentage for a step change in key variables of the capture plant.

The controller implemented in this study to maintain the key operating variables at their set point is a Linear Model Predictive Controller (LMPC). The controller requires a representation of the plant or process that accurately capture the system dynamics to extract the desired control performance. Therefore, a surrogate of the nonlinear moving bed model presented in chapter 4 is developed. A linear state space model given by Eq. (5.8) is found to be adequate. The data needed for the linear model development is obtained by subjecting the system to PRBS presented in the earlier section. Figure 5.4 compares the normalized CO₂ capture percentage obtained from linear model with Aspen Custom Modeler. Figure 5.5 shows the comparison of normalized temperature from both the models. The linear model values closely follow the ACM dynamics for both outputs,

indicating the reasonable representation that can be used in the MPC framework. The calculated MSE of the linear state space model developed using MATLAB is 0.26.

Figure 5.4 Comparison of surrogate with ACM implementation of moving bed model for capture percentage.

Figure 5.5 Comparison of surrogate with ACM implementation of moving bed model for desorber outlet temperature.

$$\begin{aligned}x(t + \Delta t) &= Ax(t) + Bu(t) \\y(t) &= Cx(t) + Du(t)\end{aligned}\tag{5.8}$$

where

$$\begin{aligned}A &= \begin{bmatrix} 0.64 & 0.37 & 0.05 & -0.0042 & -0.023 \\ 0.66 & 0.28 & -0.04 & -0.084 & -0.093 \\ 0.25 & -0.16 & 0.87 & -0.035 & -0.088 \\ 0.34 & -0.32 & -0.02 & 0.9 & -0.096 \\ 0.02 & -0.04 & 0.05 & -0.023 & 1 \end{bmatrix}; \quad B = \begin{bmatrix} -0.01 & 0.03 & 0.099 & 0.013 \\ 0.0165 & -0.064 & -0.19 & -0.022 \\ 0.012 & -0.01 & -0.06 & -0.007 \\ 0.0081 & -0.03 & -0.09 & -0.1 \\ -0.0023 & -0.005 & -0.0073 & 0.0007 \end{bmatrix}; \\ C &= \begin{bmatrix} -6.35 & -14.8 & -3.9 & 24.83 & 12.25 \\ 0.43 & -5.25 & -2.73 & 3.19 & -1.62 \\ 1.8 & 0.9 & -5.63 & 5 & -16.6 \end{bmatrix}; \quad D = [0];\end{aligned}$$

A discrete time linear state space model is found to be adequate as the soft sensor for both absorber and desorber. Figure 5.6 compares the soft sensor for the desorber for both training and validation data. The RMSE for the desorber soft sensor for training and validation data are 0.04 and 0.08 kmol/m³, respectively. The results for the absorber core H₂O soft sensor are presented in Figure 5.7. The RMSE for the absorber soft sensor for training and validation data are 0.02 and 0.025 kmol/m³ respectively.

Figure 5.6 Comparison of soft sensor for desorber outlet core H_2O with rigorous process model.

Figure 5.7 Comparison of soft sensor model for absorber outlet core H₂O with rigorous process model.

As the solvent is encapsulated in the microcapsules, it is crucial to minimize the water loss from the capsules to maintain the solvent concentration. It should also be noted that any water lost from the solvent in the regenerator consume energy. Thus, for lowering the parasitic energy loss in the regenerator, it is desired to minimize the water loss from the solvent. For controlling the water loss in the desorber, it is important to measure/estimate the water content in the encapsulated solvent at the inlet and exit of the desorber. However, as the solvent is contained within the micron-size shell, it is impractical to measure the water concentration in the solvent. In this study, a soft sensor

is developed to estimate the capsule water content by using measurements of variables that can be readily measured using the existing technology.

Performance of the controller is evaluated for both servo control and disturbance rejection characteristics. Figure 5.8 shows the servo control performance for a setpoint change of 90% to 85% in capture percentage. As the capture percentage is reduced, the amount of capsules is expected to decrease as shown in the Figure 5.8. It should be noted that the change in the capture percentage and the resulting change in the capsule serves as a disturbance to the desorber. Responses of the corresponding output and manipulated variables are not shown for brevity, but excellent performance similar to Figure 5.8 is also observed for those variables.

Figure 5.8. Transients of key variables obtained with MPC for a step change in CO₂ capture setpoint.

The flue gas flow coming to the capture plant can vary as the power output needed from the power plant changes with time. Therefore, a disturbance to the flue gas flow is introduced to understand the performance of developed control framework. Figure 5.9 presents the dynamic response of the key output variables capture percentage, desorber exit temperature, and core water content in the desorber for a 5% disturbance in the flue gas. The corresponding manipulated variables used to control is presented in the Figure 5.10. The LMPC provides a good response by avoiding the larger overshoots and longer settling times in the output variables. The soft sensors developed in this work is used for controlling the core H_2O in the desorber as shown in the Figure 5.9. Figure 5.9(c) shows the entrance and exit core H_2O values in the desorber that are calculated using the developed soft sensors. As mentioned earlier, the setpoint for exit core H_2O in the desorber is the time varying value calculated using the absorber core H_2O soft sensor. The control of exit core H_2O in the desorber to its entrance value helps in reducing the energy requirement of the process. If the desorber exit core H_2O is not controlled, the core water content leaving the desorber can go to a lower value by using more regeneration energy. The control response from the LMPC on the key outputs are compared with the traditional PID controller for the same input disturbance in flue gas flow rate. The pairing between the variables for the PID is done with the help of RGA analysis. The parameters in the PID controllers are tuned initially with the help of tuning rules available in the Aspen Custom Modeler namely, internal model control, Ziegler-Nichols, integral squared error. The parameters are manually tuned further to improve the control performance. The overshoots and the settling times are larger in the case of PID as opposed to LMPC.

Figure 5.11 presents the advantage of controlling core water content in the desorber by comparing the key process variables for a 5% disturbance in the flue gas flowrate. Figure 5.11 (a) shows the core H_2O entering and exiting the desorber and a comparison is done with the presence of soft sensor and without the soft sensor. In the case of no soft sensor, the core H_2O exiting the desorber drops to a value of 52.6 kmol/m^3 as compared to the value of 53.4 kmol/m^3 when soft sensor is used in the control framework. This loss in the water content from the core results to increase in the regeneration energy in the desorber. Figure 5.11 (b) presents the comparison of total steam flow requirements with and without the soft sensor. The total steam flow increases by almost 50% when there is no soft sensor indicating the importance of such estimation for the MECS technology. The dynamics of the capture percentage is also reported in the Figure 5.11.

Figure 5.9 Transients of outputs for a step change in flue gas flowrate.

Figure 5.10 Transients of manipulated variables for a step change in flue gas flowrate.

Figure 5.11 Comparison of key process variables with and without soft sensor using MPC.

(c)

5.5. Conclusions

In this chapter, a rigorous moving bed model for the encapsulated sodium carbonate solvent is developed. The model is used to simulate both absorption and regeneration steps of the CO₂ capture process and its sensitivity with respect to key operating conditions is studied. The correlation for heat transfer coefficient in the moving bed process is modified from the previous works which were based on fluidized bed configuration. It is observed that using the correlation based fluidized bed resulted in over prediction of heat transfer coefficient and its impact on the water dynamics in the process is presented. A techno-economic optimization framework based on the EAO of the moving bed process which accounts for both the capital and operating costs is presented. The EAO of the MECS moving bed calculated from the optimization is compared to the MEA technology and it is found that the EAO is 8% lower than the MEA in the case of 85% heat recovery.

One of the key contributions in this work is addressing the challenge of uncertainty in the encapsulated solvent concentration. A soft sensor approach is proposed in this work to estimate the state of water content in the encapsulated solvent. The methodology implemented here uses the easy to measure variables that can correlate to the solvent water content inside the microcapsule. The candidate measurement variables are the temperature and pressure at different locations in the reactor along with the process manipulated inputs. The final candidate inputs for the soft sensor are obtained by performing principal components analysis followed by a correlation evaluation. The soft sensors to estimate the exit solvent concentrations for both absorber and desorber is developed. A control framework embedding these soft sensors is developed to control CO₂ capture, desorber exit temperature, and core H₂O in the desorber. The surrogate model needed in the control framework is identified using the data from the nonlinear moving bed process in ACM. The control studies are performed by the integrating MATLAB with the Aspen Custom Modeler. The performance of LMPC is shown for the case studies involving servo control as well as disturbance rejection. A case study is presented showing the importance of soft sensor in controlling the water loss from the core.

Chapter 6. Evaluation of other Encapsulated Solvents

The MECS technology evaluated so far in the previous chapters use sodium carbonate as the encapsulated solvent. This chapter conducts the study on other possible encapsulated solvents. The concept encapsulating solvents for CO₂ capture applications can be applied to various advanced solvents that suffer from their intrinsic nature or due to complex reaction products formed after reacting with CO₂. Using the microencapsulation on these solvents can open the doors for operating these solvents in conventional reactor configuration which would have been extremely difficult otherwise.

6.1. Introduction

The potential solvents for CO₂ capture that can take advantage of encapsulation are ionic liquids, CO₂ binding organic liquids (CO₂BOLs) [80,89], and amine-based solvents to name a few. The compatibility of polymer shell with the encapsulating solvent plays a crucial role in the fabrication of microcapsules. Stolaroff et al. [13] studied the compatibility of several polymer classes for MECS production and found out couple of custom formulations, one made of silicone and another with acrylate. The intrinsic nature of ionic liquids allows the researchers to tune them according to the applications of interest [81]. The application of ionic liquids for gas separation especially in the removal of CO₂ from flue gas has been an area of study for a long time [82]. The key for economically feasible CO₂ separation technologies is to design novel solvents and ionic liquids are shown to be a good non-aqueous capture solvent [13, 83-87]. One study demonstrated a variety of capsules with ionic liquids (IL) and CO₂-binding organic liquids (CO₂BOLs) as solvents for CO₂ capture [13]. ILs are shown to be excellent solvents that can offer limitless opportunities to tailor the solvents suitable for CO₂ capture with their chemical tunability property. Such ILs are broadly defined as Task specific ionic liquids (TSIL) [87]. In TSILs, aprotic heterocyclic anions (AHA) ILs are of particular interest as they react both stoichiometrically and reversibly with CO₂ without suffering significant drawbacks due to rise in viscosities as opposed to general ILs [85,89]. The ionic liquids that exist in solid state but converts to liquid ionic complex up on reaction with CO₂ are classified as phase changing ionic liquids (PCIL). Conversely, when the CO₂ is desorbed, the liquid ionic complex turns back to solid state by releasing energy in the form of heat of fusion. This phase transition property of PCIL can help to reduce the energy requirement in the regenerator

due to the energy released via heat of fusion [86]. Another aspect of interest in pursuing ionic liquids for CO₂ capture is that they are nonvolatile and water lean solvents. This can also have significant impact on the energy requirement in the regeneration process as the energy penalty to heat water that is present in most of the aqueous solvents can be avoided. Song et al. [85] studied different encapsulated ionic liquids and phase-change ionic liquids (PCIL) and showed good recyclability of capsules. The study of these encapsulated solvents in any type of reactor is very minimal to none in the existing literature.

6.2. Encapsulated Solvent

This study investigates a TSIL, triethyl- (octyl)phosphonium 2-cyanopyrrolide - [P2228][2-CN₂Pyr]. In the representation [X][Y] of ionic liquids, X is the cation and Y is the anion. The cation characterizes the physical properties of IL such as melting point, viscosity, and thermal stability. While the anion is responsible for CO₂ reaction [91]. Phosphonium based ILs are considered over ammonium/imidazolium due to their superior thermal stability [85,86]. The tunability characteristics of ILs leads to different types and therefore the physio-chemical properties data can only be provided by the studies proposing these novel solvents for CO₂. The isotherm, properties, and kinetic data for an IL can be challenging to obtain from the open literature as most ILs are initially characterized for isotherm along with a few key physical properties. The relevant isotherm and properties data on the ILs considered here for the process modeling studies conducted is gathered from the open literature [85-87]. As mentioned earlier, the CO₂ reaction is linked to anion of the IL and the kinetic data was reported for [P₆₆₆₁₄][2CN₂Pyr] in the study [88]. The anion for this IL is similar to one of the IL considered here and therefore the same kinetic parameters can be utilized [86]. Apart from the data availability needed for process modeling, the IL considered in this study has been shown to be encapsulated [85]. Even though the microencapsulation of amine solvents is not reported in the literature yet, another capture solvent considered in this chapter is piperazine (PZ).

6.2.1. IL - Capsule Model. The capsule model presented in the chapter 2 is for the sodium carbonate solvent, representing an electrolyte system. As mentioned earlier, ionic liquids are a separate class of solvents and the reaction with CO₂ is different as compared to standard water-based solvents. The reaction happening between CO₂ and IL is represented using following mechanism

Where *CIL* is referred as ionic liquid complex and the rate expression for the above reaction is defined as [88]

$$r = k_1[CO_2][IL] \quad (6.2)$$

where $k_1 \left[\frac{L}{mol \cdot s} \right]$ is the rate constant.

The constitutive equations related to mass and energy balance will remain almost same as presented in Chapter 2 but with some minor modifications. For ease of reference, the equations are summarized here. The species transfer from the bulk gas phase to capsule surface is given as

$$N_{i,G} = k_{i,G}(C_{i,G,bulk} - C_{i,shell}) \quad (6.3)$$

The species transfer from the surface to the shell can be characterized through diffusion as

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{i,shell} r^2 \frac{\partial C_{i,shell}}{\partial r} \right) = 0 \quad (6.4)$$

The liquid side flux in the capsule can be described through enhancement factor as

$$N_{i,L} = Ek_{i,L}(C_{tot,L}x_{i,int} - C_{i,core}) \quad (6.5)$$

The enhancement factor along with the component balance equations are shown below

$$E = Ha = \frac{\sqrt{k_1 C_{IL} D_{CO_2}}}{k_{i,L}} \quad (6.6)$$

The chemistry model for the ionic liquids can be found below:

$$C_{CO_2,core} = C_{CO_2,core}^* + C_{CIL} \quad (6.7)$$

$$C_{IL,core} = C_{IL,core}^* + C_{CIL} \quad (6.8)$$

$$C_{tot,L} = C_{IL,core}^* + C_{CO_2,core}^* + C_{CIL} \quad (6.9)$$

The underlying sub models that characterize the CO₂ reacting with encapsulated solvent plays an important role and all the relevant models like isotherm, reaction, and property models related to ionic liquids are presented in the Appendix D.

6.2.1. PZ - Capsule Model. Piperazine is a secondary amine consisting of two amine branches, thus can provide larger capacities for CO₂ capture [92]. However, it is observed experimentally that PZ reacting with CO₂ can precipitate especially at lower temperatures and lean loading loadings [93,94]. The formation of precipitates can have significant impact on the capture process as they can lead to operational issues like clogging, difficulty in solvent circulation and so on. Several studies have been performed in characterizing the PZ system and proposing innovative reactor configurations to deal with the precipitation issues and energy requirements [95-98]. Microencapsulation technology can be helpful to address the precipitation issues often seen in amine-based capture solvents due to the formation of bicarbonates up on reacting with CO₂ [95].

The capsule model for the PZ solvent is similar to the one presented in chapter 2 for sodium carbonate solvent. However, the kinetics, chemistry and properties model are modified accordingly for PZ system. The reaction of CO₂ with PZ is well studied in the literature and the main reactions of PZ-CO₂-H₂O system can be described using [93, 97]

The elementary balance to predict the equilibrium concentration of species can be written as follows:

$$C_{PZ,L} = C_{PZ,L}^* + C_{PZCOO^-} + C_{PZCOO^{2-}} + C_{HPZCOO} + C_{PZH^+} \quad (6.17)$$

$$C_{CO_2,L} = C_{CO_2,L}^* + C_{HCO_3^-} + C_{PZCOO^-} + C_{PZCOO^{2-}} + C_{HPZCOO} + C_{CO_3^{2-}} \quad (6.18)$$

$$C_{H_2O,L} = C_{H_2O,L}^* + C_{HCO_3^-} + C_{H_3O^+} + C_{OH^-} + C_{HPZCOO} + C_{PZH^+} \quad (6.19)$$

$$C_{H_3O^+} + C_{PZH^+} = C_{HCO_3^-} + C_{PZCOO^-} + C_{OH^-} + 2C_{PZCOO^{2-}} + 2C_{CO_3^{2-}} \quad (6.20)$$

$$C_{Liq} = C_{CO_2,L} + C_{PZ,L} + C_{H_2O,L} \quad (6.21)$$

The VLE model developed for PZ-CO₂-H₂O system is validated with the limited data available in the open literature [93]. Figure 6.1 compares the model results with the experimental data for 2 m PZ (~14 wt%) solvent at 40°C and 60°C. Figure 6.1 shows the change in CO₂ loading plotted on x-axis with increase in the partial pressure of CO₂ plotted on y-axis.

Figure 6.1. VLE comparison between model and experimental data for PZ solvent.

6.3. Modeling and Techno-Economic Analysis

The performance studies of encapsulated ionic liquids in any reactor configuration for the CO₂ capture applications is not seen in the literature. This section presents the fixed bed modeling results of ionic liquid and PZ solvent discussed earlier. The modeling equations of fixed bed reactor shown in the chapter 3 are modified for the case of encapsulated ionic liquids. The bulk level mass balance equations for the gas phase and its interaction with the capsule model remains same. However, the energy balance equations are written in terms of temperature variable instead of enthalpy. The gas phase energy balance is

$$\epsilon_{bed} c_{p,g} \frac{\partial(C_{T,G} T_g)}{\partial t} = -c_p \frac{\partial(u_G C_{T,G} T_g)}{\partial z} - (1 - \epsilon_{bed}) a_{e, cap} h_{gs} (T_g - T_s) + a_{e, hx} h_{hxwG} (T_{hxw} - T_g) \quad (6.22)$$

The core energy balance is

$$c_{p,c} \frac{\partial(C_{T,L} T_c)}{\partial t} = h_c a_e (T_s - T_c) + a_e N_{CO_2,L} \Delta H_{rxn} \quad (6.23)$$

The flue gas conditions, and reactor configuration specifications are kept to same values used for the encapsulated sodium carbonate solvent and it can be found chapter 3. The diffusion of water through the polymer for encapsulated ionic liquid is not considered in this analysis. The fixed bed studies similar to encapsulated sodium carbonate solvent is also performed on both ionic liquid and piperazine solvent. For ionic liquid, the impact of residence time on the key operating variables such as breakthrough time, desorption time, and the number of beds required is presented in the Table 6.1.

Table 6.1 Impact of residence time on the number of beds and cycle times for ionic liquid

Residence time (τ) (s)	Breakthrough time (t_b) (s)	Desorption time (s)	Absorption beds	Total beds in the cycle
59	1589	1117	16	28
66	2799	1245	20	29
100	7522	1432	37	45
200	20554	1510	89	96

The decrease in flue gas residence time corresponds to higher superficial velocity which means larger amounts of flue gas can be processed in a single reactor. Therefore, the number of parallel

absorption beds needed will keep decreasing as the residence time decreases. As more CO₂ is loaded in the bed at higher breakthrough times, the regeneration energy needed for the process will be lower. However, the corresponding total number of parallel beds required is more as shown in the Table 6.1 indicating the larger capital cost. Therefore, an economic analysis taking both capital and operating costs of the process is performed. Figure 6.2 shows the breakthrough curve for ionic liquid.

Figure 6.2 Breakthrough curve for encapsulated ionic liquid at a residence time of 100 s.

Figure 6.3 shows the CO₂ loading profiles for the encapsulated ionic liquid at different locations of the fixed bed reactor. As the CO₂ gets absorbed by the ionic liquid, the release of heat of absorption results in the temperature rise of the bed. This rise in temperature results in a poor CO₂ loading at later sections of the bed as captured by the middle and end portions of the reactor. The incoming flue gas helps to reduce the temperature at the entrance section where the CO₂ loading increases to certain extent with respect to time as compare to the rest of the bed. The effect of having a heat removal mechanism during the absorption is not studied here but it can improve the overall CO₂ bed loading. Ionic liquids are hygroscopic and can be a problem to the performance of ionic liquids as it can impact the absorption of CO₂ chemistry [87]. As mentioned before, the impact of water on the performance of ionic liquids is not considered here and should be taken up as an improvement to the analysis shown in this study.

Figure 6.3 CO₂ loading profiles for encapsulated ionic liquid at different locations of the fixed bed, residence time of 100 s.

The impact of operating conditions such as flue gas residence time and initial bed temperature on the process economics is evaluated. The specifications related to the technoeconomic analysis like the plant life, interest rate, and equipment costing methodology is presented in the section 3.4. Figure 6.4 shows the equivalent annual operating cost, EOAC for the encapsulated ionic liquid in a carbon steel type of reactor. The EAOC values are better for lower initial bed temperatures as the CO₂ capacity of ionic liquids is better at low temperatures. The isotherm profiles for the task specific ionic liquids can be seen in the Appendix D. The sensitivity with respect to residence time is also captured in Figure 6.4, where the EAOC values increase with residence time. This is due to the rise in capital cost attributed to the total number of parallel fixed beds required to process the flue gas as shown in Table 6.1. Figure 6.5 presents the EAOC for the encapsulated ionic liquid in a concrete reactor. The EAOC values are compared to the standard MEA system for both material of construction in the case of 85 % heat recovery. It can be seen that the EAOC of encapsulated ionic liquid performs better than the MEA system for concrete based reactor. The initial bed temperature of 25°C and concrete reactor type results in an improvement of approximately 9 % in the EAOC over MEA system.

Figure 6.4 Impact of the residence time on the EAOOC of encapsulated ionic liquid for various initial bed temperatures with carbon steel as the material of construction for the beds.

Figure 6.5 Impact of the residence time on the EAOOC of encapsulated ionic liquid for various initial bed temperatures with concrete as the material of construction for the beds.

The third and final solvent considered here is piperazine with an assumption that this can encapsulated, even though there are no experimental studies on the same for now. Table 6.2 presents the sensitivity with respect to residence time on the encapsulated 40 wt.% PZ solvent for an initial bed temperature of 40°C.

Table 6.2. Impact of residence time on the number of beds and cycle times for PZ

Residence time (τ) (s)	Breakthrough time (t_b) (s)	Desorption time (s)	Absorption beds	Total beds in the cycle
40	1501	3479	7	24
50	3428	3690	12	25
66	7332	3833	20	31
100	15585	3900	38	48

The reactivity of CO₂ with amines is faster compared to carbonate solvents and it can be seen from requirement of the number of parallel beds. Due to this high reactivity, the reactor can be operated at high gas velocities which results in a lower number of parallel absorption beds for processing the flue gas coming from the power plant. The total number of fixed beds almost reduces by 1/4th for PZ as compared to sodium carbonate. However, it should be noted that the heat of absorption of CO₂ for amines is almost three times compared to carbonate solvents. Therefore, an analysis based on capital and operating costs is presented later. Figure 6.6 presents the breakthrough curve of encapsulated PZ solvent.

Figure 6.6 Breakthrough curve for encapsulated PZ at a residence time of 75 s.

Figure 6.7 shows the loading profiles of encapsulated PZ solvent at different sections of the fixed bed reactor.

Figure 6.7. CO₂ loading profiles for encapsulated PZ at different locations of the fixed bed, residence time of 75 s.

Figure 6.8 presents the EAOc values of PZ for carbon steel type of reactor at three different initial bed temperatures. The EAOc values are better if the bed is operated at lower temperatures as shown in the Figure 6.8. In the case of sodium carbonate solvent, the EAOc values were also evaluated at initial bed temperatures of 40°C, 60°C, and 80°C. However, it is observed that operating the bed at 60°C is economical. The less reactive nature of carbonate solvents with CO₂ [36] requires the temperature to be high compared to PZ solvent which are highly reactive towards CO₂. For encapsulated PZ solvent, the EAOc value reduces approximately by 50% compared to sodium carbonate solvent in the case of carbon steel type of reactor. Figure 6.9 represents the EAOc of PZ for concrete based reactor and the EAOc value is improved by 44% as compare to sodium carbonate solvent. The EAOc value of PZ is almost same as the standard MEA system for the concrete reactor. The EAOc values shown in Figures 6.8 and 6.9 are based on 85 % heat recovery.

Figure 6.8 Impact of the residence time on the EAOC of encapsulated PZ for various initial bed temperatures with carbon steel as the material of construction for the beds.

Figure 6.9 Impact of the residence time on the EAOC of encapsulated PZ for various initial bed temperatures with concrete as the material of construction for the beds.

6.4. Conclusions

The fixed bed analysis performed on encapsulated sodium carbonate solvent is extended to two different types of solvents, one is ionic liquid, and another is piperazine with 40 wt.% concentration. The isotherm, kinetic, and physio-chemical property sub models of ionic liquid needed for this work is gathered from the literature [85-88, 91]. The kinetics and equilibrium constants of the PZ solvent is taken from the literature [94-98]. The VLE model implemented for PZ solvent is validated with the literature data. The capsule model is modified accordingly for both the solvents to accurately capture the microscale behavior. An EAOE based analysis is performed on both the solvents and compared against sodium carbonate solvent. The sensitivity of EAOE with respect to flue gas residence time for three different initial bed temperatures are done on both solvents. It is found that EAOE values of both the solvents outperformed Na_2CO_3 for all the operating conditions. The number of parallel beds which contributes to the capital cost of the process is relatively higher for Na_2CO_3 solvent. In the case of PZ, the EAOE value for 85% heat recovery is same as the standard MEA solvent when concrete is used as reactor construction material. For the combination of ionic liquid and concrete as reactor type, the EAOE is 9% better than the MEA solvent. However, the fixed bed analysis using encapsulated ionic liquid did not consider the impact of water.

For both ionic liquid and PZ, the lower operating temperatures are found to be favorable in the overall reduction of EAOE. However, in the case of sodium carbonate solvent the operating temperature needs to be higher compared to the other solvents to reach an optimum EAOE due to the low reactivity of CO_2 with Na_2CO_3 . The analysis informs that the performance of MECS in a fixed bed type of reactor depends on the combination of various components. The encapsulated solvent plays a significant role along with the operating temperature to reduce the amount of EAOE of the process. Another sensitivity presented on the economics of the process is with respect to the construction of material for reactor. The operation of MECS using the highly reactive solvents in a moving bed reactor type of configuration can result in further improvements in the economics.

Chapter 7. Future work

The multiscale models developed here for the evaluation of MECS technology can be further improved with the help of experimental studies. First, the capsule level experiments with an aim of characterizing the water diffusion through the polymer shell should be done. In this study, the mass transfer parameter for water through the shell is taken from the literature. The experimental studies analyzing impact of encapsulated solvent on the mass transfer of both CO₂ and water through the shell is also lacking. The operating conditions such as solvent concentration, temperature, and composition of the gas mixture should be varied over a range of values while conducting the experimental studies. The data can then be used to estimate the polymer shell mass transfer parameters of these components which is crucial in assessing the performance of microcapsules. In the case of sodium carbonate solvents, the VLE data for higher solvent concentrations is not available to validate the equilibrium model predictions. Another crucial sub-model for which no information was available in the open literature is heat of absorption as a function of CO₂ loading. Therefore, experimental studies on sodium carbonate solvent to obtain the data for these components can increase the reliability on the scale up studies. Second, the experimental studies on a reactor scale of any configuration can be helpful in characterizing the mass, heat, and hydrodynamics behavior of the microcapsules through estimation of model parameters.

The capsule model in this study is characterized and validated using the experimental data on sodium carbonate solvent for the temperatures up to 60°C. The capsule model validation should be extended to regeneration temperatures up to 120°C. The optimization of fixed bed model simulating the cyclic operation can be considered as an extension of the fixed bed analysis conducted here. The dynamics of the heat recovery from the fixed bed is not implemented and can be seen as improvement on the current version of the model. The techno-economic analysis conducted here is based on the scale up correlations and the information from Aspen Process Economic Analyzer (APEA). There is a scope in improving the capital cost estimates and it may be achieved by contacting equipment vendors. The contribution of sodium carbonate-based capsules cost in the total capital cost of the fixed bed process varies between 1 % to 2 % depending on the number of reactors, material of construction, and initial bed temperature. The fixed bed model implemented in this study needs to be characterized using the experimental data of any

scale. The improvements to the moving bed model should be focused on the incorporating the hydrodynamics in a more rigorous way, may be using experimental studies. The modeling studies inform that the MECS technology in a moving bed configuration can be promising but the practical implementation needs to be evaluated to identify the operational challenges of the process. One of the challenges addressed here is the estimation of encapsulated solvent concentration that can help to inform the capsule status as well as optimize the energy requirements by reducing the water loss. The soft sensor used here is a linear model and studies related to the impact of nonlinear model on the predictions can be included in the future work. The moving bed model identification can be extended to include another input flue gas CO₂ composition. The output variable CO₂ capture rate disturbance range in the identified linear model presented in this work varies from 78 % – 94 %. The disturbance in flue gas flow and CO₂ composition together can result in the capture percentage to go down further and the existing linear model may not be suitable. The reduced order model can be further improved to account for such disturbances. Further, the control framework can be extended from LMPC to NLMPC to see the impact on the control performance.

The sensitivity of encapsulated solvent is analyzed here through modeling studies for two other solvents, ionic liquid and PZ. The impact of water diffusion on the performance of ionic liquid is not considered in this study. When the water transport is included in the analysis, the sub-models like isotherm, kinetics, and physio-chemical properties should be updated first before conducting the reactor level studies. The modeling studies can be taken up for other solvents such as phase changing ionic liquids and CO₂-binding organic liquids that can take advantage of the microencapsulation.

Appendix

Appendix A: Microcapsule model boundary conditions

The mass balance boundary conditions for the capsule at the shell surface and at the interface of core liquid and shell are given by:

$$D_{i,shell} \frac{\partial C_{i,shell}}{\partial r} = N_{i,G} \quad (A.1)$$

$$D_{i,shell} \frac{\partial C_{i,shell}}{\partial r} = N_{i,L} \quad (A.2)$$

where i denotes H₂O and CO₂. The corresponding equations for both the fluxes are given as

$$N_{i,G} = k_{i,G}(C_{i,G} - C_{i,shell}) \quad (A.3)$$

$$N_{i,L} = Ek_{i,L}C_{T,L}(x_{i,int} - x_i^*) \quad (A.4)$$

The energy balance boundary conditions for the capsule are given by

$$-K_{shell} \frac{\partial T_s}{\partial r} = h_c(T_c - T_s) \quad (A.5)$$

$$-K_{shell} \frac{\partial T_s}{\partial r} = h_{gs}(T_s - T_g) \quad (A.6)$$

Appendix B: Fixed Bed Correlations and EAO

This section presents important correlations, and boundary conditions used for the fixed bed reactor model. The EAO values for both concrete and carbon-steel reactors with varying temperatures, residence times, and heat recovery percentages are presented in Table B.

Correlations for heat and mass transfer coefficients used in the fixed bed model

The mass transfer coefficient between the gas and to the surface of the shell is given as [99]

$$Sh = 2 + 1.1Re^{0.6}Sc^{1/3} = \frac{k_g d_p}{D_g} \quad (B.1)$$

The heat transfer coefficient between fluid and particle h_{gs} is obtained from Nusselt number correlation [99]

$$Nu_{gs} = 2 + 1.1Re^{0.6}Pr^{1/3} = \frac{h_{gs} d_p}{K_g} \quad (B.2)$$

The condensation (or average) heat transfer coefficient can be predicted by the correlation given as below [100]

$$h_{hxw} = 1.137 \left(\frac{g\rho_{cl}(\rho_{cl} - \rho_v)h_{fg}k_{cl}^3}{\mu_{cl}(T_{sat} - T_{hxw})l_b} \right)^{0.25} \quad (B.3)$$

The heat transfer coefficient between the packed bed and the immersed heat exchanger tubes is given as [101]

$$Nu_{hxwG} = (0.33 + 0.26Re_{d_{hxt}}^{0.533})Pr^{\frac{1}{3}}\left(\frac{d_{hxt}}{d_{cap}}\right)^{0.1} = \frac{h_{hxwG}d_{hxt}}{K_{eff}} \quad (B.4)$$

Fixed bed reactor boundary conditions

Gas Phase

$$\text{At } z = 0 \quad u_{G,in}C_{i,G,in} = u_G C_{i,G} \quad H_{G,in} = H_G \quad \frac{\partial T_{hxw}}{\partial Z} = 0 \quad (B.5)$$

$$\text{At } z = L \quad \frac{\partial C_{i,G}}{\partial Z} = 0 \quad \frac{\partial T_{hxw}}{\partial Z} = 0 \quad \frac{\partial H_G}{\partial Z} = 0 \quad (B.6)$$

Table B. EAO for different extent of heat recovery, material of construction, and different initial bed temperatures.

Temperature (°C)	Material	Residence time (s)	EAO (\$ million) for different heat recovery percentages					
			Zero	50%	60%	75%	85%	90%
40	Concrete	75	2735	1464	1210	828	701	574
		100	1652	956	817	608	539	469
		150	1292	791	690	540	490	440
		200	1255	791	699	559	513	467
	Carbon-steel	75	3021	1750	1495	1114	987	860
		100	1891	1196	1056	848	778	709
		150	1565	1063	963	812	762	712
		200	1584	1120	1027	888	842	795
60	Concrete	50	2242	1233	1032	729	628	527
		66	1510	886	762	574	512	450
		100	1277	782	683	535	485	436
		200	1318	849	755	614	568	521
	Carbon-steel	50	2486	1477	1275	973	872	771
		66	1718	1094	970	783	720	658
		100	1512	1017	918	770	720	671
		200	1702	1233	1139	998	951	905
80	Concrete	40	1713	1013	873	663	593	523
		50	1494	906	788	612	553	494
		66	1409	878	772	612	559	506
		100	1391	891	792	642	592	542
		200	1633	1101	995	835	782	729
	Carbon-steel	40	1925	1226	1086	876	806	736
		50	1700	1112	994	818	759	700
		66	1642	1111	1005	845	792	739
		100	1687	1188	1088	938	888	838
		200	2172	1640	1534	1374	1321	1268

Appendix C: MATLAB and ACM Integration

The LMPC control and soft sensors are developed in MATLAB/Simulink and the moving bed model is implemented in Aspen Custom Modeler V8.4. Both software's are connected through to perform the control studies. The link to ACM V8.4 from the MATLAB will be successful only via 32-bit application and the MATLAB version used here is 2015b. Once the correct version of software is installed, the following snippet of code needs to be executed in the command window.

"C:\Program Files (x86)\AspenTech\AMSystem V8.4\Bin\AMSimulink.dll"

The above command is for ACM V8.4, so it needs to be changed accordingly to the version for which link is being set up. More details can be found in the customer support website of Aspen Plus.

Appendix D: Ionic Liquid Isotherm and Property Models

[P2228][2CNPyr] is task specific ionic liquid (TSIL) is shown to be a promising ENIL. The VLE model is given as [85]

$$Z \left(\frac{\text{mol } CO_2}{\text{mol IL}} \right) = \frac{P_{CO_2}}{H} + c \frac{K_{eq} P_{CO_2}}{1 + K_{eq} P_{CO_2}} \quad (D.1)$$

$$\ln(K_{eq}) = \left(-\frac{\Delta H_{rxn}^0}{RT} \right) + \left(\frac{\Delta S_{rxn}^0}{R} \right) \quad (D.2)$$

Table D. Parameters for the Isotherm Model

Ionic Liquid	Parameter	Value	Units
[P2228][2CNPyr]	ΔH_{rxn}^0	-46.6 ± 1.1	kJ/mol
	ΔS_{rxn}^0	-127 ± 3	J/molK

Diffusivity:

The diffusivity of CO₂ in ionic liquids can be calculated using the correlation suggested by [102]

$$D_{CO_2,IL} = 3.7e^{-6} \mu_{IL}^{-0.4} MW_{IL}^{0.4} \rho_{IL}^{-1.6} \quad (D.3)$$

Where $D_{CO_2,IL}$ in cm²/s, viscosity in cP, and density in g/cc

Density:

The correlation equation for density as a function of temperature (10°C-70°C) for [P2228][2-CNPyr] is given as (g/cc) [91]

$$\rho = AT + B \quad (D.4)$$

where A = -5.58e-4 g/cc/K and B = 1.122 g/cc.

Viscosity:

The viscosity of ILs can be represented using VFT equation [91]

$$\eta = \eta_o \exp\left(\frac{\alpha}{T - T_g}\right) \quad (D.5)$$

Where $\eta_o(\text{cP}) = 0.042$, $\alpha = 1110 \text{ K}$, and $T_g = 167 \text{ K}$

Heat capacity:

The correlation equation for heat capacity (C_p) as a function of temperature (25°C-65°C) for [P66614][2-CNPyrr] is given as (J/mol °C) [87]

$$C_p = AT + B \quad (D.6)$$

where as $A = 1.89 \text{ (J/mol } ^\circ\text{C}^2)$ and $B = 1147 \text{ (J/mol } ^\circ\text{C})$

Heat of reaction:

The heat of reaction (ΔH_{rxn}) of CO_2 with [P2228][2-CNPyrr] is -46.6 kJ/mol [87]

Figure D. Comparison of isotherm model implementation with the literature data.

Appendix E: Publications and Presentations

Selected Presentations:

1. Goutham Kotamreddy, Ryan Hughes, Benjamin Omell, Michael Matuszewski, Debangsu Bhattacharyya, '*Dynamic Modeling, Optimization, and Control Studies of a Moving Bed Process for CO₂ Capture Using a Micro-Encapsulated Solvent*', AIChE 2020.
2. Goutham Kotamreddy, Ryan Hughes, Joshua Stolaroff, Katherine Hornbostel, Benjamin Omell, Michael Matuszewski, Debangsu Bhattacharyya, '*Process Modeling and Techno-Economic Analysis of Fixed Bed System using Micro-Encapsulated Solvent for CO₂ Capture*', AIChE 2019.
3. Goutham Kotamreddy, Ryan Hughes, Joshua Stolaroff, Benjamin Omell, Michael Matuszewski, Debangsu Bhattacharyya, '*Process Modeling and Techno-Economic Analysis of Moving Bed System using Micro-Encapsulated Solvent for CO₂ Capture*', AIChE 2019.
4. Goutham Kotamreddy, Debangsu Bhattacharyya, Joshua Stolaroff, Michael Matuszewski, Ryan Hughes, '*Process Modeling and Experimental Studies of a Novel Micro-Encapsulated Solvent System for CO₂ Capture*', AIChE 2017.
5. Ryan Hughes, Goutham Kotamreddy, Debangsu Bhattacharyya, Michael Matuszewski, '*Process Modeling and Optimization of a Novel Membrane-Assisted Chilled Ammonia Process for CO₂ Capture*', AIChE 2017.

Publications:

1. Goutham Kotamreddy, Ryan Hughes, Debangsu Bhattacharyya, Michael Matuszewski, and Benjamin Omell, *Moving Beds for Carbon Capture Using Microencapsulated Carbon Sorbents: Part 1. Moving Bed Modeling and Techno-Economic Optimization*, Internal Review.
2. Goutham Kotamreddy, Ryan Hughes, Debangsu Bhattacharyya, Michael Matuszewski, and Benjamin Omell, *Moving Beds for Carbon Capture Using Microencapsulated Carbon Sorbents: Part 2. Soft Sensor Development and Model Predictive Control*, Internal Review.
3. Goutham Kotamreddy, Ryan Hughes, Debangsu Bhattacharyya, Joshua Stolaroff, Katherine Hornbostel, Michael Matuszewski, and Benjamin Omell, *Process Modeling and Techno-*

Economic Analysis of a CO₂ Capture Process Using Fixed Bed Reactors with a Microencapsulated Solvent, Energy & Fuels 2019 33 (8), 7534-7549.

4. Chirag Mevawala, Xinwei Bai, Goutham Kotamreddy, Debangsu Bhattacharyya, and Jianli Hu, *Multiscale Modeling of a Direct Nonoxidative Methane Dehydroaromatization Reactor with a Validated Model for Catalyst Deactivation*, Industrial & Engineering Chemistry Research 2021 60 (13), 4903-4918.
5. Ryan Hughes, Goutham Kotamreddy, Anca Ostace, Debangsu Bhattacharyya, Rebecca L. Siegelman, Surya T. Parker, Stephanie A. Didas, Jeffrey R. Long, Benjamin Omell, and Michael Matuszewski, *Isotherm, Kinetic, Process Modeling, and Techno-Economic Analysis of a Diamine-Appended Metal–Organic Framework for CO₂ Capture Using Fixed Bed Contactors*, Energy & Fuels 2021 35 (7), 6040-6055.
6. Ryan Hughes; Goutham Kotamreddy; Benjamin Omell; Michael Matuszewski, Debangsu Bhattacharyya, *Process Modeling and Bayesian Uncertainty Quantification of a Novel Membrane-Assisted Chilled Ammonia Process for CO₂ Capture*, International Journal of Greenhouse Gas Control, Submitted.

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