

Active Temperature Control Strategy in Adsorption-based Carbon Capture Process for Minimum Exergy Losses[#]

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ABSTRACT

Adsorption-based carbon capture is a promising carbon reduction technology for combating climate change. However, the desorption of CO₂ from the adsorbent demands a high energy input, which limits this technology's further development. In the desorption step of a temperature swing adsorption (TSA) cycle, the heat transfer from the heat source to the adsorbent and the mass transfer of CO₂ from the adsorption phase to the gas phase inevitably leads to exergy losses. Moreover, both heat and mass transfer are typically initially fast and then slow down, as the imbalance potential differences starting large but decreasing over time. The initial large potential differences accelerate the process but cause significant exergy losses. A more uniform potential difference distribution over the entire time scale is expected to achieve better balance between the exergy losses and desorption time. In this regard, this study proposes an active control strategy, that is, regulating the potential difference by process temperature control to reduce exergy losses. A one-dimensional numerical model for carbon capture was established to validate the proposed strategy. The optimal temperature-time condition was identified for a case study to guide the process design. The exergy demand of desorption step is reduced effectively under the active temperature control strategy. This study aims to minimize the exergy losses thereby contribute to the large-scale deployment of adsorption-based carbon capture.

Keywords: carbon capture, adsorption, climate change, exergy, entropy

NONMENCLATURE

Abbreviations

CCS	Carbon capture and storage
COP	Performance coefficient
PAT	Process average temperature

TSA	Temperature swing adsorption
<i>Symbols</i>	
b	Adsorption equilibrium constant
c_p	Specific heat capacity (J·K ⁻¹ ·kg ⁻¹)
E	Exergy (J)
G	Gibbs free energy (J)
k	Mass transfer coefficient
L	Length of adsorption chamber (m)
LW	Lost work (J)
n	Adsorbed amount (mol/kg)
P	Pressure (pa)
R	Ideal gas constant (J·K ⁻¹ ·mol ⁻¹)
s	Entropy (J/K)
S	Heat transfer area (m ² /m ³)
t	Time (s)
T	Temperature (K)
U	Heat transfer coefficient J/(m ² s K)
v	Velocity (m/s)
W	Work (J)
y	Concentration of CO ₂
p	Partial pressure of component (pa)
ϵ	Bed void fraction
ΔH	Adsorption heat (J/mol)

1. INTRODUCTION

Facing to the grim situation of global warming, great efforts must be made to mitigate the greenhouse effect. Carbon capture and storage (CCS) technology is widely regarded as a prospective solution for controlling climate change and achieving the negative emissions of CO₂. Various technical CCS technologies including absorption, adsorption, membrane, and cryogenic have been proposed. Particularly, the adsorption technology with solid adsorbents for cyclic CO₂ capture is a promising method owing to a low energy penalty for regeneration and low capital investment^[1].

However, the substantial energy cost of adsorption technology still constitutes its greatest challenge and constrains its further application. To overcome this

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bottleneck, scholars have made great efforts in material development, mechanism exploration and process design. On the one hand, in order to achieve the best balances between separation performance and energy consumption, a series of process parameters including adsorption and desorption temperature, desorption time, inlet concentration and inlet rate have been widely explored and optimized. On the other hand, exploring the energy conversion mechanism in the carbon capture process is also helpful to improve energy efficiency. A series of theoretical models based on classical thermodynamic methods, such as separation models, process-based models, and carbon pump models, have been established to analyze the energy conversion mechanism in carbon capture. Some corresponding energy efficiency performance indicators such as minimum separation work, CO₂ performance coefficient (COP), and second law efficiency have also been proposed to evaluate energy efficiency. Furthermore, non-equilibrium thermodynamic methods can further explore the energy conversion mechanism in carbon capture systems. For example, Guo Zhihao et al.^[2] used non-equilibrium thermodynamic methods to identify the irreversible factors in adsorption-based carbon capture and analyzed the composition, mechanism and quantification method of the entropy sources in the system.

Existing energy efficiency researches provide guidance from a theoretical perspective. Furthermore, the idea of non-equilibrium thermodynamics is expected to be directly applied to the process design, thus reducing the irreversibility of the system and saving energy. For a typical adsorption carbon capture process, namely the temperature swing adsorption cycle (TSA), there are many irreversible factors that cause exergy loss, including heat transfer, mass transfer, flow resistance, dissipation, etc. Among these factors, the major ones are the irreversible heat transfer process between the cold heat source and the adsorption chamber and the irreversible mass transfer process of CO₂ between the adsorption phase and the bulk gas phase. Regulating these irreversible processes can effectively reduce exergy loss. Moreover, optimizing the desorption step, which is the most energy consuming step, can reduce exergy loss more directly. For the desorption step, the temperature difference between the heat source and the adsorbents and the chemical potential difference between the adsorption phase and the gas phase drive the heat and mass transfer process. These unbalanced potentials are typically large initially but decrease over time. Excessive potential differences

accelerate the process but also bring about large irreversible losses. The above-mentioned heat transfer temperature difference and mass transfer chemical potential difference are both dominated by the heat source temperature. Therefore, regulating the temperature of the external heat source is expected to adjust the unbalanced potential difference in the process, thereby reducing irreversible losses.

Currently, constant-temperature heat source is often utilized to drive the desorption step. This paper proposes an active control strategy instead of a constant temperature for the heat source, which could regulate the desorption process and ultimately reduces the exergy loss of the entire carbon capture cycle. A fast-calculation nonequilibrium carbon capture mathematical model is established, and the nonequilibrium thermodynamic method is applied to perform relevant energy analysis.

2. METHOD

2.1 Model establishment and process description

As shown in Figure 1, a simplified temperature-swing adsorption-desorption cycle is considered in this study. The cycle consists of two steps: alternating heating desorption and cooling adsorption. For the heating desorption step, the adsorbent is heated from room temperature T_{atm} to the desorption end temperature $T_{heatend}$. Under the thermal drive, the adsorbed CO₂ is desorbed from the adsorption phase to the gas phase and flows out of the adsorption chamber; For the cooling adsorption step, the adsorbent is cooled by cooling water at room temperature T_{atm} . At the same time, the simulated flue gas (N₂/CO₂) with a CO₂ concentration of y_{feed} enters the adsorption chamber at a speed of v_{feed} . The gas components therein are adsorbed to a certain extent and then flow out of the adsorption chamber as waste gases.

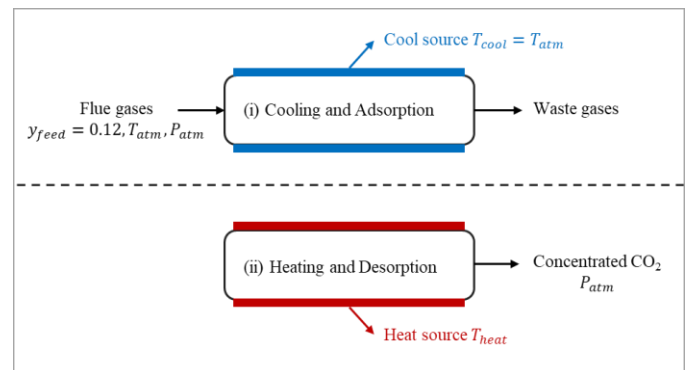


Fig. 1 The scheme for TSA process

Adsorbent zeolite 13X was selected as the adsorption material. As a representative physical adsorption material, it has a large CO₂ adsorption capacity and a small N₂ adsorption capacity. The relevant thermodynamic and kinetic adsorption properties have been reported by many literature^[3].

The cycle parameter settings are listed in Table 1. Moreover, the following assumptions and simplifications are made to carry out the numerical simulation:

(1) The gas phase is regarded as an ideal gas;

(2) The flow pressure drop as well as the specific heat capacity of the adsorption phase are ignored.

(3) The axial and radial mass diffusion and heat diffusion are ignored. The adsorption bed is regarded as a zero-dimensional structure.

(4) Parameters such as heat transfer coefficient and specific heat capacity are regarded as constants.

Table 1 Parameter Used for the Simulations

Parameters	Value	Description
y_{feed}	0.12	CO ₂ content in flue gases
T_{atm}	298 K	Room temperature
P_{atm}	1 bar	Atmospheric pressure
ϵ	0.70	Bed void fraction
S	133.5	Heat transfer area
U	16.8 J/(m ² s K)	Heat transfer coefficient
v_{feed}	0.5 m/s	Inlet velocity
C_p	920	[4]
K_1	0.0035	[5]
K_2	0.003	[5]
$\Delta H_1(\text{CO}_2)$	-37000 J/mol	Clausius-Clapeyron ^[6]
$\Delta H_2(\text{N}_2)$	-18510 J/mol	Clausius-Clapeyron ^[6]

2.2 Governing equation

The adsorption behavior is described by the thermodynamic and kinetic function. The adsorption amount at equilibrium state is calculated by a competitive isotherm using the extended binary Sips equation^[7]:

$$n_{i,e} = n_{i,ref} \frac{(b_i p_i)^{c_i}}{1 + \sum_{i=1}^2 (b_i p_i)^{c_i}} \quad (1)$$

Where the p_i represents the partial pressure of component i . $n_{i,ref}$ and b_i are the saturation capacity and adsorption equilibrium constant. The third parameter c_i accounts for the surface inhomogeneity.

The kinetic property is described by the pseudo-first order model:

$$\frac{\partial n_i}{\partial t} = k_i(n_{i,e} - n_i) \quad (2)$$

Where n_i is actual adsorbed amount, and k_i is the mass transfer coefficient.

For the heating and desorption step, the mass conservations are described by the equation (3-4).

$$\frac{\epsilon P}{R} \frac{d\left(\frac{y}{T}\right)}{dt} - \rho \frac{dn_1}{dt} + \frac{v_{out} y P}{L RT} = 0 \quad (3)$$

$$\frac{\epsilon P}{R} \frac{d\left(\frac{1}{T}\right)}{dt} + \rho \frac{dn_1}{dt} + \rho \frac{dn_2}{dt} + \frac{v_{out} P}{L RT} = 0 \quad (4)$$

By eliminating the v_{out} term in the equation (3-4), the equation (5) is obtained as:

$$\frac{\epsilon P}{RT} \frac{dy}{dt} + \rho(1-y) \frac{dn_1}{dt} - y\rho \frac{dn_2}{dt} = 0 \quad (5)$$

Substituting Equation (2) into (5), the equation (6) is obtained:

$$\frac{dy}{dt} = \frac{RT}{\epsilon_t P} (-\rho k_1(1-y)(n_{1e} - n_1) + \rho k_2 y(n_{2e} - n_2)) \quad (6)$$

The energy conservation equation is described as equation (7):

$$c_b \frac{dT}{dt} - \rho \sum_{i=1}^2 (-\Delta H_i) \frac{\partial n_i}{\partial t} = US(T_{heat} - T) \quad (7)$$

Substituting equation (2) into (7), the equation (8) is obtained:

$$\frac{dT}{dt} = \frac{(US(T_{heat} - T) - \Delta H_1 k_1 \rho (n_{1e} - n_1) - \Delta H_2 k_2 \rho (n_{2e} - n_2))}{c_b} \quad (8)$$

Similarly, the energy conservation equation for the cooling and adsorption is written as:

$$\frac{dT}{dt} = \frac{(US(T_{cool} - T) - \Delta H_1 k_1 \rho (n_{1e} - n_1) - \Delta H_2 k_2 \rho (n_{2e} - n_2))}{c_b} \quad (9)$$

And the mass conservation equations for the cooling and desorption are described by equations (10-11):

$$\frac{\epsilon_t P}{R} \frac{d\left(\frac{y}{T}\right)}{dt} + \rho \frac{dn_1}{dt} + \frac{\epsilon_t v_{out} y P}{L RT} - y_{feed} \frac{\epsilon_t v_{in} P}{L RT} = 0 \quad (10)$$

$$\frac{\epsilon_t P}{R} \frac{d\left(\frac{1}{T}\right)}{dt} + \rho \frac{dn_1}{dt} + \rho \frac{dn_2}{dt} + \frac{\epsilon_t v_{out} P}{L RT} - \frac{\epsilon_t v_{in} P}{L RT} = 0 \quad (11)$$

After eliminating the v_{in} term in equations (10-11) which represents the inlet speed of feed gases, the equation is rewritten as:

$$\frac{dy}{dt} = \frac{RT}{\epsilon_t P} (-\rho k_1(1-y)(n_{1e} - n_1) + \rho k_2 y(n_{2e} - n_2)) + (y_{feed} - y) \frac{v_{in}}{L} \quad (12)$$

2.3 Exergy analysis

In the simplified non-equilibrium model, other irreversible factors such as flow resistance, dissipation, etc. are ignored. Only two primarily irreversible processes are analyzed. That is, the heat transfer process between the cold and heat source and the adsorption

chamber, and the mass transfer process of CO₂ between the gas phase and the adsorption phase. Based on the classical thermodynamic exergy equilibrium analysis method, for a single adsorption and desorption cycle, its exergy equilibrium is written as equation (13):

$$\Delta E = E_{input} - W_{min} - T_{atm}S_g \quad (13)$$

Among them, E_{input} is the exergy input in a single cycle, which is provided by the heat source in this study. W_{min} is the minimum separation work done in a single cycle, which represents the theoretical work to separate CO₂ from the mixed gas. S_g is the total entropy production of one cycle, and $T_{atm}S_g$ is the exergy loss of the cycle.

The calculation method of thermal exergy and minimum separation work is as shown in equation (14-15):

$$dE_{input} = \left(1 - \frac{T_{atm}}{T_{heat}}\right) dQ \quad (14)$$

$$W_{min} = n_2G_2 + n_3G_3 - n_1G_1 \quad (15)$$

Equation (16) gives the calculation method of the total entropy generation of the system, which is divided into heat and mass transfer losses. In addition, both heating desorption and cooling adsorption would cause heat and mass transfer losses.

$$S_g = S_{heat} + S_{mass} \quad (16)$$

The entropy generated from heat transfer is calculated as:

$$dS_{heat} = US(T_{heat} - PAT) \left(\frac{1}{PAT} - \frac{1}{T_{heat}} \right) dt \quad (17)$$

The entropy generated from mass transfer is calculated as:

$$dS_{mass} = -R \ln \left(\frac{P}{P_{eq}} \right) dn \quad (18)$$

The specific energy consumption is calculated as:

$$E_{spec} = \frac{E_{input}}{n_s} \quad (19)$$

The energy efficiency is calculated as:

$$\eta = \frac{W_{min}}{W_{ac}} = \frac{W_{min}}{W_{min} + LW} \quad (20)$$

The exergy balance on the system is described as:

$$E_{input} = T_{atm}(S_{heat} + S_{mass}) + W_{min} + \varepsilon \quad (21)$$

3. RESULTS AND DISCUSSIONS

According to the idea of using different heat source temperatures to control exergy losses, four different strategies were compared and the heat and mass transfer processes and the exergy equilibrium for these strategies were analyzed. To ensure the comparability of the strategies, the adsorption and desorption times were uniformly set as 5000 s and 3000 s, respectively. The adsorbent temperature at the end of the desorption step was equal. The heat and mass transfer processes of the

desorption step of the four strategies are shown in Figure 2.

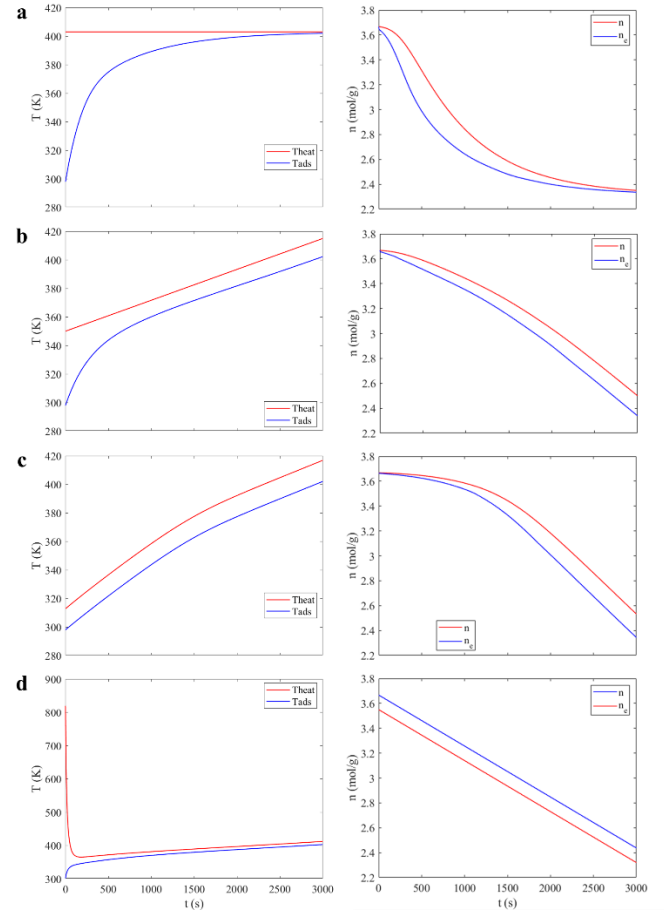


Fig. 2 The heat and mass transfer process for different strategies. (a) constant heating temperature (b) heating temperature increasing linearly with time (c) maintaining a pinch point for temperature difference (d) maintaining a pinch point for chemical potential difference

2.1 Exergy analysis

The strategy of constant heating temperature is set as the baseline. Taking E_{sepc} as the optimization target, the optimized desorption temperature of 403.12 K is solved by the sqp algorithm. At this temperature of 403 K, a single TSA cycle can separate 1.32 mol CO₂, with a total exergy input of 2.71E+07 J and an exergy efficiency of 17.4%. The exergy losses of four strategies for separating 1 mol CO₂ are demonstrated in Figure 3. It can be observed that most of the input heat exergy is dissipated in the form of exergy losses, of which heat transfer losses accounts for the vast majority (92.67%), and mass transfer accounts for only 7.33%. Therefore, the irreversible heat transfer should be highlighted for regulation and exergy loss reduction.

2.2 Comparison of different heat source regulation strategies

Taking the constant heating temperature of 403 K as the benchmark (Strategy a), the other three heat source regulation strategies are compared. Drawing on the method of narrow point temperature difference in heat transfer, that is, maintaining the minimum narrow point potential difference in the irreversible process to reduce exergy loss, the strategy of narrow point heat transfer temperature difference and mass transfer potential difference is proposed (Strategy b and c). In addition, a simple scenario of linear increase in heat source temperature is also proposed for comparison (Strategy d). Compared with the benchmark, the narrow point heat transfer and mass transfer strategies reduce 65.3% of heat transfer exergy loss and 46.7% of mass transfer exergy loss, respectively. However, the narrow point mass transfer method amplifies the heat transfer exergy loss, thus leading to a decrease in overall exergy efficiency. Therefore, the optimization of exergy loss should focus on the heat transfer process.

The four strategies are ranked from high to low in terms of exergy efficiency: narrow point heat transfer, linear increase in heat source temperature, constant temperature heat source, and narrow point mass transfer. Under reasonable process design, the active temperature control strategy can effectively reduce energy consumption and improve efficiency. Compared to the benchmark strategy, the heat transfer narrow point strategy reduces the specific energy consumption by 17.36%.

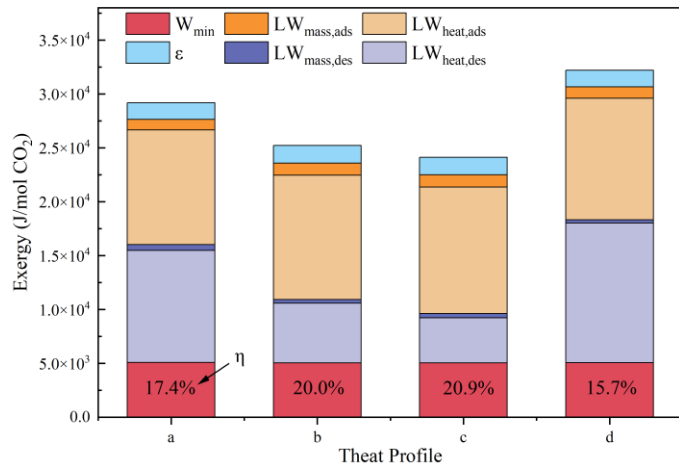


Fig. 3 The exergy distribution under different temperature control strategies

4 CONCLUSIONS

This paper proposes an active temperature control strategy for carbon capture, which controls the

irreversible heat and mass transfer process by actively adjusting the temperature of the heat source in the desorption step. A zero-dimensional nonequilibrium carbon capture model is established for a simplified TSA cycle, enabling rapid calculations of the physical fields associated with carbon capture. Four control strategies are proposed and the nonequilibrium thermodynamic method is used to analyze their exergy loss. The results show that the exergy loss of adsorption carbon capture is mainly caused by the irreversible heat transfer between the cold heat source and the adsorption chamber. The exergy loss of irreversible mass transfer of CO₂ between the adsorption phase and the gas phase only accounts for a small proportion. By applying a heat source with a temperature that changes with time, the energy efficiency can be effectively improved. The approach of maintaining the minimum heat transfer narrow point and the minimum mass transfer narrow point can reduce the heat transfer exergy loss by 65.3% and the mass transfer exergy loss by 46.7%, respectively. Among the four strategies, the strategy of maintaining the heat transfer narrow point has the smallest exergy loss, and its exergy efficiency is increased from 17.4% to 20.9% compared to the baseline. The implementation of a dynamic heat source effectively reduce the irreversibility of the desorption process, the corresponding process design is thereby helpful for carbon capture energy saving.

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