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Performance exploration of temperature swing adsorption technology for carbon dioxide capture

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Abstract: Adsorption technology is recognised to be a promising CO₂ capture method due to its desirable characteristics e.g. reusable nature of adsorbents, low capital investment and easy automatic operation. To further improve thermal performance, internal heat recovery is adopted for adsorption CO₂ capture through analogy with adsorption refrigeration. Based on carbon pump theory, thermal performance of 4-step temperature swing adsorption (TSA) processes is analysed at various adsorption/desorption temperatures and pressures. Exergy efficiency of adsorption CO₂ capture with and without heat recovery will be evaluated and compared by using experimental adsorption characteristics of activated carbon. Metal part and unused percentage of adsorption reactor are defined to further assess their influence on system performance in real application. Results indicate that sensible heat of adsorbents and adsorbed phase account for the major part of heat consumption. For different desorption/adsorption temperatures and pressures, theoretical exergy efficiency of 4-step TSA cycle ranges from 0.022 to 0.221. Heat recovery is conducive to exergy efficiency. Through heat recovery, exergy efficiency could be improved from 54.3% to 84.6% when mass ratio increases from 0 to 8. Similarly, the improvement by using heat recovery is up to 90% in terms of different unused percentages.

Keywords: Carbon capture; Temperature swing adsorption; Carbon pump; Exergy efficiency

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22 Nomenclature

Activated carbon	AC
CCS	Carbon capture and storage
E	Exergy (kJ)
H	Reaction heat ($\text{kJ}^{-1} \cdot \text{kg}^{-1}$)
MOF	Metal organic framework
m	Mass (kg)
P	Pressure (Pa)
PSA	Pressure swing adsorption
Q	Heat (kJ)
q	CO_2 adsorption capacity ($\text{kg}^{-1} \cdot \text{kg}^{-1}$)
Re	Recovery
T	Temperature ($^{\circ}\text{C}$)
TSA	Temperature swing adsorption
VSA	Vacuum swing adsorption
W	Work ($\text{kJ}^{-1} \cdot \text{kg}^{-1}$)
WC	Working capacity ($\text{kg}^{-1} \cdot \text{kg}^{-1}$)
y	CO_2 concentration

23 Greek letters

η	Efficiency
ψ	Percentage

24 Subscripts

ad	Adsorption
CO_2	Carbon dioxide
c	Cooling
con	Condensation
de	Desorption
ex	Exergy
H	High temperature

h	Heating
hr	Heat recovery
i	Ideal
L	Latent heat
l	Low temperature
max	Maximum
min	Minimum
r	Real
re	Reactor
S	Shaft work
s	Sensible
sat	Saturation

25

26 **1. Introduction**

27 Carbon capture and storage (CCS) has been gathering the momentum, which aims to prevent the
 28 release of large quantities of carbon dioxide (CO₂) to the atmosphere since it is considered to mitigate
 29 the contribution of fossil fuel emissions to global warming and ocean acidification [1]. Carbon capture
 30 technologies could be realized by three main methods: pre-combustion capture, post-combustion
 31 capture and oxyfuel combustion [2]. Among them, post-combustion capture plays a leading role due to
 32 the advantage of retrofitting existing industrial stations. Post-combustion capture could be achieved
 33 through a variety of methods e.g. cryogenic, membrane, adsorption, absorption process, etc. [3].

34 Absorption is once considered as the most likely commercialized technology for CO₂ capture.
 35 Nonetheless, energy penalty for large-scale application is also considerable [4]. It is extensively
 36 acknowledged that absorption and adsorption have many similarities. Solid adsorbents have several
 37 advantages e.g. low capital investment, easy to control, reversible characteristics, which ensure a
 38 relatively good performance for CO₂ capture [5]. Selection of adsorbents is one of major methods to
 39 improve the overall efficiency of CO₂ adsorption process. Materials i.e. zeolite 5A, zeolite 13X,
 40 activated carbon (AC) and silica gel have been widely investigated for adsorption refrigeration and
 41 CO₂ capture [6, 7]. Several novel materials e.g. metal organic framework (MOF) have once aroused
 42 burgeoning attentions due to large adsorption capacity and high gas selectivity [8]. Nevertheless, the

cost is correspondingly higher than that of other classical materials. Comprehensively considering cost, adsorption capacity and thermal stability, AC is one of the most suitable aspirants for CO₂ capture, which is inexpensive and insensitive to moisture with a high surface area [9]. Adsorption isotherms and reaction heat of AC have been ensured by various researchers [10, 11]. The clear thermal properties are quite helpful to understand adsorption phenomenon, which could be used for system design and optimization of CO₂ capture. Except for selection of adsorbent, different operation methods i.e. thermal adsorption cycles also determine the performance of CO₂ capture.

Through the variation of temperature or pressure, approaches to adsorption CO₂ capture could be classified into pressure swing adsorption (PSA) and temperature swing adsorption (TSA). PSA operates adsorption process at a pressure higher than atmosphere value while vacuum swing adsorption (VSA) is defined when adsorption process proceeds at atmospheric pressure and desorption happens under a low pressure. Considering TSA, adsorption reactor is usually heated by a feed of hot medium e.g. hot water or steam, and then adsorption reactor is cooled by cooling medium e.g. cooling water before next adsorption cycle. For PSA and TSA, the minimum separation work is commonly used for evaluating thermodynamic performance of CO₂ capture, which only provides a quantity of work for separating process. Under this scenario, it could be regarded as an evaluation index when other external conditions e.g. input work, heating temperature and environmental temperature are mutually similar [12]. Recently, compared to heat pump theory, a novel term of carbon pump was proposed to realize an enrichment of CO₂ from carbon source to carbon sink, which aims to evaluate energy efficiency for CO₂ capture technologies. This concept provides an insightful direction to reveal thermal performance of CCS technologies [13]. Later, comparisons of thermal efficiencies among various carbon capture methods were conducted based on carbon pump theory [14].

Generally speaking, adsorption cycles could be developed for various functions. Air conditioning and freezing lie in different output temperatures of evaporator [15]; Heat pump and storage could transform thermal energy into chemical potential and then supply heat with a higher temperature [16, 17]; Desiccant and desalination act as open systems for adsorption and desorption process [18, 19]; Power generation and cogeneration have a higher energy grade output by integrating an expander [20, 21], etc. One remarkable fact is that continuous efforts are made for various adsorption cycles in the progress of improving thermal efficiency. Thus thermal cycles of adsorption refrigeration and heat pump are also various with their unique advantages. Heat recovery is usually adopted for exchanging

the heat between adsorption reactors with different temperatures whereas mass recovery is used for balancing pressure difference between adsorption reactors [22]; Thermal wave cycle utilizes a simple heat transfer fluid loop for a high energy efficiency [23]; Two-stage cycle aims to reduce heat source temperature by adding another adsorption reactor [24]; Resorption cycle has a higher refrigeration efficiency by using desorption heat as cooling effect [25]. Since carbon pump is analogous to heat pump, various improved cycles e.g. heat recovery cycle could also be expected to improve thermal efficiency of carbon pump cycle, which is advantageous to the performance of carbon capture technology. For adsorption refrigeration and heat pump, heat and mass recovery are commonly used to improve the performance of a basic adsorption cycle [26]. With regard to carbon pump, it tends to consider that heat recovery is suitable for TSA process and mass recovery for PSA process due to their respective temperature and pressure difference.

In this paper, heat and mass recovery are first proposed for adsorption carbon capture cycle. A detailed analysis is conducted to illustrate the influence of heat recovery on thermal efficiency of 4-step TSA cycle based on carbon pump theory. The minimum separation work and exergy efficiency of 4-step TSA cycle are determined by using the experimental characteristics of AC. Under the condition of different adsorption/desorption temperatures and pressures, thermal efficiency with heat recovery will be compared with that not using heat recovery for detailed illustration. Metal part and unused percentage of adsorption reactor are also assessed, which is substantial for real application.

2. Working principles of adsorption cycles

Fig.1 indicates schematic diagram of a basic 4-step TSA cycle, which is based on carbon pump theory [13]. Several assumptions of the cycle are described as follows: 1) Temperature inside the adsorbent is uniform, i.e. no temperature gradient exists in different directions. 2) Adsorbent has little adsorption capacity of N_2 when compared with adsorption capacity of CO_2 , i.e. N_2 is only used as a purge gas. 3) CO_2 is evenly distributed in each process of the cycle, i.e. filling method and structure of adsorption reactor are not considered. The cycle is thermodynamically composed of four working processes i.e. adsorption, preheating, desorption and precooling. Fig.1a shows the process schematic of each adsorption reactor while Fig.1b demonstrates thermodynamic diagram, which contains pressure, temperature and CO_2 adsorption capacity. The details of each step are illustrated as follows:

Step 1-2 is an adsorption process. In this process, gas mixture i.e. N_2/CO_2 flows into adsorption

reactor. Then CO_2 is adsorbed by adsorbent, and cooling medium will take away adsorption heat. This could correspond to thermodynamic process from point 1 to point 2. It is worth noting that theoretical adsorption process could be at point 5 i.e. saturation adsorption point. Due to the limit of external condition in real application e.g. structure of adsorption reactor, constraint temperature and dead volume, adsorption process cannot reach point 5.

Step 2-3 is a preheating process. After adsorption process, adsorption reactor is immediately heated by heating medium e.g. hot steam. During the preheating process, temperature of adsorption reactor is increased but no CO_2 is desorbed, which could correspond to thermodynamic process from point 2 to point 3.

Step 3-4 is a desorption process. Temperature of adsorption reactor is increased and N_2 purge is used sequentially. After temperature reaching T_3 of point 3, CO_2 adsorption capacity for the reactor is higher than the maximum value with the increasing temperature at a constant pressure P_{de} . Then desorption process of CO_2 begins, and CO_2 with a high concentration flows out of adsorption reactor until temperature of adsorption reactor reaches T_4 . This could correspond to thermodynamic process from point 3 to point 4.

Step 4-1 is a precooling process. Cooling medium flows into the inner tube for removing the heat from adsorption reactor. Until temperature of reactor decreasing to T_1 , the operation conditions are resumed hereafter and a new 4-step TSA cycle is started. This could correspond to thermodynamic process from point 4 to point 1.

(a)

(b)

Fig.1. Schematic diagram for 4-step TSA cycle (a) process schematic; (b) adsorption isotherm diagram.

Fig.2 indicates Clapeyron diagram of a typical physical adsorption refrigeration cycle, which is often used to clearly illustrate adsorption and desorption process. Cycle 2-3-4-1-2 is plotted in terms of adsorption reactor whereas cycle 2-3-5-6-2 is depicted with regard to refrigerant. Since 4-step TSA cycle for CO₂ capture is essentially an adsorption cycle, analogy could be conducted between adsorption refrigeration cycle and TSA cycle. By using the same coordinates, Clapeyron schematic of 4-step TSA cycle is shown in Fig.3, which is corresponding to each process in Fig.1. The main difference is that 4-step TSA cycle isn't considered as a close cycle in terms of working fluid, thus working cycle of CO₂ is not described in Fig.3. One remarkable fact is that in real application, process 4-1 and 1-2 proceed at the same time and process 2-3 and 3-4 happen simultaneously i.e. desorption proceeds with heating process whereas adsorption proceeds with cooling process.

Fig.2. Clapeyron diagram of typical physical adsorption refrigeration cycle.

Fig.3. Clapeyron diagram of 4-step TSA Cycle for CO₂ capture.

As it is mentioned in introduction, heat and mass transfer recovery are commonly used for improving the performance of adsorption refrigeration. After adsorption and desorption process have been finished respectively, one adsorption reactor has a high temperature which requires precooling whereas the other has a low temperature and prepares preheating. Sensible heat and reaction heat of adsorbent are able to be recovered via a closed heat exchange circuit. Theoretically, 4-step TSA cycle could realize internal heat recovery between 1-2-3 and 3-4-1 process as shown in Fig.4. In real operation, heat recovery begins when one reactor finishes adsorption at point 1, and the other reactor finishes desorption at point 3. Thus only the sensible heat of adsorption reactor could be recovered.

In this case, heat input is decreased owing to the increase of desorption capacity and the decrease of start desorption temperature. This may result in the increase of exergy efficiency.

Case 4: Fig.5d demonstrates cycle characteristic of 4-step TSA cycle in terms of different adsorption temperatures. When adsorption temperature increases from 293 K to 303 K, 4-step TSA cycle will change from 1-2-3-4-1 to 1-2'-3'-4-1. The adsorption capacity decreases sharply with the increase of adsorption temperature, which is not conducive to CO₂ capture.

It is worth noting that four cases in Fig.5 are described as theoretical situation i.e. unused percentage of adsorption reactor is assumed as 0 and metal part is not taken into account. Thus point 2 is at the adsorption line. Four cases correspond to the change of each side of rectangle 1-2-3-4-1 under certain adsorption and desorption reaction lines. If unused percentage of adsorption reactor is considered as shown in Fig.6, point 2 will turn to point 2'. In this case, desorption capacity decreases which will lead to a higher energy input and a lower exergy efficiency.

Fig.5. Cycle characteristics of 4-step TSA cycle in terms of various (a) desorption pressures; (b) desorption temperatures; (c) adsorption pressures; (d) adsorption temperatures.

196

197 Fig.6. Cycle characteristic of 4-step TSA cycle with regard to unused percentages of adsorption reactor.

198

199 **3. Analytical methodology of 4-step TSA cycle**

200 According to Fig.1b, working capacity (WC) and unused percentage of adsorption reactor could be
 201 expressed as following equation 1-3, in which WC_i is the ideal working capacity and WC_r is the real
 202 working capacity.

$$WC_i = q_5 - q_1 \quad (1)$$

$$WC_r = q_2 - q_1 \quad (2)$$

$$\psi_{un} = 1 - \frac{q_2}{q_5} \quad (3)$$

203 where q_1 , q_2 and q_5 are adsorption capacity of point 1, 2 and 5 in Fig.1b.

204 CO_2 recovery rate (Re_{CO_2}) is usually defined to evaluate CO_2 separation performance, which could
 205 be expressed as equation 4. In regard of equation 3, equation 4 could be transferred into equation 5. If
 206 external conditions i.e. adsorption/desorption temperatures and pressures are ensured, Re_{CO_2} is only
 207 related with the unused percentage of adsorption reactor. It is evident that two parameters reveal a
 208 reverse trend i.e. Re_{CO_2} increases with the decrease of unused percentage of adsorption reactor [27].

$$Re_{CO_2} = \frac{WC_r}{WC_i} = \frac{q_2 - q_1}{q_5 - q_1} \quad (4)$$

$$Re_{CO_2} = 1 - \frac{\psi_{un} q_5}{q_5 - q_1} \quad (5)$$

209 The minimum separation work (W_{min}) for carbon capture system could be calculated by Gibbs

equation as a state function which is independent of thermal process. According to carbon pump theory, $W_{\min}$ is only relevant with three parameters i.e. heat input temperature T_{in} , CO_2 fraction (y_{CO_2}) and Re_{CO_2} , which could be expressed as equation 6.

$$W_{\min} = G(T_{\text{in}}, y_{\text{CO}_2}, Re_{\text{CO}_2}) \quad (6)$$

Exergy efficiency is the ratio of the minimum separation work to actual work (W_r). Therefore, exergy efficiency is defined as equation 7, which could refer to the reference [28]:

$$\eta_{\text{ex}} = \frac{W_{\min}}{W_r} = \frac{W_{\min}}{W_{\min} + W_{\text{loss}}} = \frac{W_{\min}}{W_s + Q_H \left(1 - \frac{T_0}{T_H}\right) - Q_L \left(1 - \frac{T_0}{T_L}\right)} \quad (7)$$

where W_s is input work, Q_H is heat input of high temperature heat source, Q_L is heat output of low temperature heat source, T_L is adsorption temperature, T_H is desorption temperature. Adsorption and desorption temperature are defined as the average temperature in reaction process. W_s is not considered in 4-step TSA process because of no extra power apparatus.

In equation 7, Q_H i.e. heat input for 4-step TSA cycle is composed of latent heat i.e. reaction heat and sensible heat with regard to mass of captured CO_2 . It could be expressed as equation 8:

$$\begin{aligned} Q_H &= (Q_{s,\text{CO}_2} + Q_{s,\text{ad}} + Q_{s,\text{re}} + Q_{L,\text{ad}})/(q_3 - q_4) \\ &= (Q_{s,\text{CO}_2} + Q_{s,\text{ad}} + Q_{s,\text{re}})/(q_3 - q_4) + H_{\text{ad}} \end{aligned} \quad (8)$$

where the first term in the right side of equation 8 is sensible heat consumed by adsorbed phase of CO_2 , the second and third term are sensible heat consumed by adsorbent and sorption reactor, respectively. The fourth term is reaction heat. q_3 and q_4 are desorption capacity of point 3 and 4 in Fig. 1b.

Heat recovery in this paper is analyzed theoretically, which indicates that T_{hr} is the average value of T_h and T_L . After heat recovery, heat input of 4-step TSA cycle is reduced as expressed equation 9.

$$Q'_H = (Q_{s,\text{CO}_2} + Q_{s,\text{ad}} + Q_{s,\text{re}} + Q_{s,L} - Q_{\text{hr}})/(q_3 - q_4) \quad (9)$$

where Q_{hr} is the sensible heat of adsorbents and adsorption reactor which could be recovered in heat recovery process.

4. Results and discussions

4.1 Theoretical performance

This part aims to evaluate theoretical performance of 4-step TSA cycle based on thermodynamic properties of AC. Four cases as discussed above could be analysed and classified into desorption and

adsorption processes, i.e. desorption pressure and temperature varies in case 1 and 2 while adsorption parameters varies in case 3 and 4. Performance without considering heat recovery process is first discussed, then it is compared with that using heat recovery process. Afterwards unused percentage of adsorption reactor and mass ratio between adsorption reactor and adsorbent are adopted for assessing the performance in real application.

Fig.7 demonstrates thermal performance of 4-step TSA cycle in terms of heat input, actual work and the minimum separation work. Unused percentage of adsorption reactor is assumed as 0. For clear comparison of energy consumption, four CO₂ partial pressures for desorption i.e. as 0.03 MPa, 0.04 MPa, 0.05 MPa and 0.06 MPa are adopted as shown in Fig.7a. Other conditions e.g. adsorption pressure and desorption temperature are controlled as the same which could refer to case 1 in Fig.5a. Both cycle heat input and work are evaluated with regard to per kilogram CO₂ for consistency. It is worth noting that both heat input Q_H and actual work W_r increase with the increase of CO₂ partial pressure for desorption. This is mainly because desorption capacity i.e. q_3-q_4 decreases with the increase of CO₂ partial pressure for desorption, which causes the considerable increase of heat input according to equation 8. Although adsorption reaction heat slightly decreases when pressure increases from 0.03 MPa to 0.06 MPa as shown Table 1, sensible heat takes a leading role, which is higher than adsorption heat with several orders of magnitude. Since desorption temperature and environmental temperature don't change, actual work has a similar trend with heat input. The minimum separation work W_{min} is constant since three parameters i.e. T_{in} , y_{CO_2} and Re_{CO_2} don't change at various CO₂ partial pressures for desorption according to equation 6. Similarly, four desorption temperatures i.e. 328 K, 338 K, 348 K and 358 K are adopted for comparison as indicated in Fig.7b. Other conditions e.g. adsorption pressure, adsorption temperature are controlled as the same which could refer to case 2 in Fig.5b. It is demonstrated that heat input decreases with the increase of desorption temperature due to the rise of desorption capacity. Sensible heat declines with the increase of desorption temperature. Different from the situation at various CO₂ partial pressures for desorption, reaction heat of adsorbent increases with the increase of desorption temperature, but it still has little influence on heat input. One remarkable fact is that actual work decreases from 328 K to 348 K and then increases from 348 K to 358 K owing to the increase of desorption temperature. The minimum separation work doesn't change with the increase of desorption temperature due to the fact that it is related with T_{in} , y_{CO_2} and Re_{CO_2} according to equation 6. Since these three parameters don't change at different desorption temperatures,

the minimum separation work keeps constant.

Fig.7. Thermal performance of 4-step TSA cycle under the condition of (a) different CO₂ partial pressures for desorption; (b) different desorption temperatures.

Table 1. Reaction heat of AC at different CO₂ partial pressures and temperatures [29].

Partial pressure of CO ₂ (MPa)	Temperature (K)					
	358	348	338	303	293	283
Reaction heat (kJ ⁻¹ ·kg _{CO₂} ⁻¹)						
0.02	27.5	26.6	25.8	20.7	23.6	24.6
0.03	26.3	25.6	24.7	19.7	22.7	23.7
0.04	25.4	24.7	23.9	19.1	22.1	23.1
0.05	24.8	24.1	23.4	18.5	21.6	22.6
0.06	24.3	23.6	22.9	18.1	21.1	22.2

Based on the minimum separation work and actual work, exergy efficiencies are then evaluated in terms of various CO₂ partial pressures and temperatures. Fig.8 indicates exergy efficiency of 4-step TSA cycle under the condition of 0.03-0.06 MPa CO₂ partial pressure for desorption and 328-358 K desorption temperature. Results show that exergy efficiency decreases with the increase of desorption pressure. When desorption temperature increases, exergy efficiency increases first then decreases. The

highest exergy efficiency of 4-step TSA cycle is able to reach 0.221 which could be obtained at 348 K desorption temperature and 0.03 MPa CO₂ partial pressure for desorption. The lowest value is about 0.04 at 328 K desorption temperature and 0.06 MPa CO₂ partial pressure for desorption. It tends to select the optimal desorption temperature and control CO₂ partial pressure for desorption as low as possible. Nevertheless, it could control the best desorption temperature in real application. Since CO₂ partial pressure for adsorption has a limited range from 0.01 MPa to 0.02 MPa i.e. feed gas of CO₂ accounts for 10% to 20% after power plant, CO₂ partial pressure for desorption is difficult to be controlled accurately when it is close to CO₂ partial pressure for adsorption. Through similar calculation, exergy efficiency at different adsorption temperatures and CO₂ partial pressures for adsorption could be obtained, which is indicated in Fig.9. As mentioned above, CO₂ partial pressure for adsorption are selected as 0.01 MPa, 0.015 MPa and 0.02 MPa according to case 3 in Fig.5c. Since adsorption temperature is close to environmental temperature, temperatures of 293 K, 298 K and 303 K are selected for further illustration according to case 4 in Fig.5d. It could be observed that exergy efficiency increases with the increase of CO₂ partial pressure for adsorption. This could be mainly attributed to the fact that sensible heat input decreases sharply with the increase of CO₂ partial pressure for adsorption. Thus actual work is correspondingly reduced due to the same desorption temperature and environmental temperature. The minimum separation work decreases slightly with the increase of CO₂ partial pressure for adsorption due to the increase of CO₂ fraction y_{CO_2} . Also worth noting that exergy efficiency increases with the decrease of adsorption temperature. For various adsorption temperatures and CO₂ partial pressures for adsorption, the highest exergy efficiency of 4-step TSA cycle is able to reach 0.22 which could be obtained at the lowest adsorption temperature i.e. 293 K and the highest CO₂ partial pressure for adsorption i.e. 0.02 MPa due to the simple variation trend of exergy

efficiency and selected temperature and pressure range. For similar reasons, the lowest value could be obtained 0.022 at 303 K and 0.01 MPa. In real application, adsorption temperatures and CO_2 partial pressures for adsorption are determined by post combustion carbon capture of power plant and environmental cooling medium, which could not be varied greatly.

Fig.8. Exergy efficiency of 4-step TSA cycle with regard to different CO_2 partial pressures for desorption and temperatures.

Fig.9. Exergy efficiency of 4-step TSA cycle with regard to different adsorption temperatures and CO_2 partial pressures for adsorption.

309

310 4.2 Performance of 4-step TSA cycle with heat recovery process

311 Performance of 4-step TSA cycle with heat recovery is further elaborated in this part which is also
 312 compared with that not using heat recovery process. The actual work and exergy efficiency with and
 313 without heat recovery are compared in terms of various desorption temperatures and CO₂ partial
 314 pressures for desorption, which are shown in Fig.10. It is demonstrated that heat recovery is quite
 315 advantageous to thermal performance of 4-step TSA cycle. As shown in Fig.10a, the actual work could
 316 be reduced by up to 44.5% and exergy efficiency could be improved by up to 76.4%. Also worth noting
 317 that exergy efficiency with heat recovery becomes close to that without heat recovery when CO₂ partial
 318 pressure for desorption increases from 0.03 MPa to 0.06 MPa. In regard of different desorption
 319 temperatures, heat recovery also plays a significant role on thermal efficiency. When desorption
 320 temperature ranges from 328 K to 358 K, the actual work could be reduced by up to 41.1% and exergy
 321 efficiency could be improved by 67.3%. Similarly, exergy efficiency of 4-step TSA cycle with and
 322 without heat recovery are also assessed under the conditions of various adsorption temperatures and
 323 CO₂ partial pressures for adsorption which are as shown in Fig.11. When CO₂ partial pressure for
 324 adsorption increases from 0.01 MPa to 0.02 MPa, the improvement by using heat recovery could reach
 325 up to 76%. Similarly, difference of exergy efficiency with and without heat recovery increases sharply
 326 when adsorption temperature increases from 293 K to 303 K. The highest improvement is about 115%
 327 at adsorption temperature of 303 K. It is worth noting that heat recovery is more advantageous to
 328 thermal performance under some relatively severe conditions e.g. desorption and adsorption
 329 temperature are 358 K and 303 K or CO₂ partial pressure for desorption and adsorption are 0.03 MPa
 330 and 0.01 MPa, respectively.

331

(a)

(b)

Fig.10. Actual work and exergy efficiency of 4-step TSA cycle under the condition of (a) different CO_2 partial pressures for desorption; (b) different desorption temperatures.

Fig.11. Exergy efficiency of 4-step TSA cycle under the condition of (a) different CO_2 partial pressures for adsorption; (b) adsorption temperatures.

4.3 Influence of metal part and unused percentage of adsorption reactor

This section aims to investigate the influence of metal part and unused percentage of adsorption reactor on thermal performance of 4-step TSA cycle in real application. Unused percentage of adsorption reactor is adopted to evaluate the usage efficiency of adsorption reactor. Since Re_{CO_2} is below 0 when unused percentage is larger than 40% according to equation 5, percentage of 0, 10%, 20% and 30% are selected for detailed comparison and further analysis, which could refer to Fig.6.

Fig.12a indicates heat input, actual work and the minimum separation work in terms of different unused percentages of adsorption reactor. It is obvious that heat input increases with the increase of unused percentage due to the fact that desorption/adsorption capacity correspondingly decreases with the increase of unused percentage. In regard of growing unused percentage of adsorption reactor, actual work also increases remarkably due to the fact that desorption temperature and environmental

temperature doesn't change. The minimum separation work decreases with the increase of unused percentage due to the reduced CO₂ recovery rate. Fig.12b shows CO₂ recovery rate, exergy efficiency in terms of different unused percentages. According to equation 5, CO₂ recovery rate demonstrates a reverse trend with unused percentage of adsorption reactor. When the unused percentage increases from 0 to 30%, CO₂ recovery rate linearly decreases from 1 to 0.32. Exergy efficiency with and without using heat recovery are also compared. When unused percentage of adsorption reactor increases from 0 to 30%, exergy efficiency with and without heat recovery decreases from 0.312 to 0.09 and from 0.167 to 0.048. The improvement by using heat recovery is up to 90% in terms of different unused percentages.

Fig.12. Thermal performance of 4-step TSA cycle with regard to different unused percentages of adsorption reactor (a) heat input and work; (b) exergy efficiency and CO₂ recovery rate.

Except for unused part of adsorption reactor, mass ratio is also usually used to evaluate thermal performance in real application, which is defined as the specific value between mass of sorption reactor and adsorbent i.e. mass of metal part divided by total mass of adsorbent. Exergy efficiency of 4-step

TSA cycle in terms of different mass ratios is presented in Fig.13. It is indicated that mass ratio has a remarkable influence on exergy efficiency due to the increased heat input of adsorption reactor. With the increased heat exergy input of metal part, exergy efficiency decreases with the increase of mass ratio. When mass ratio increases from 0 to 8, exergy efficiency of 4-step TSA cycle without heat recovery varies from 0.167 to 0.023, which is decreased by 86.5%. Heat recovery could be more conducive to exergy efficiency of systems with high mass ratios. Through heat recovery, exergy efficiency could be improved from 54.3% to 84.6% when mass ratio increases from 0 to 8. For adsorption refrigeration, mass ratio between adsorbent and adsorption reactor is usually higher than 3 [30]. However, considering the system for CO₂ capture, mass ratio could be controlled between 1 and 2. Even in this case, the improvement of exergy efficiency by using heat recovery could reach about 70%.

Fig.13. Exergy efficiency of 4-step TSA cycle with and without heat recovery in terms of different mass ratios between adsorption reactor and adsorbent.

According to the references [13, 31], exergy efficiency of post CO₂ capture technologies could be

classified into two groups. Exergy efficiency of the first group is above 15%, and absorption and adsorption technology could be the representatives. The second group could reach exergy efficiencies of approximately 10% or even lower, which includes processes such as cryogenic separation. Heat recovery proposed for 4-step TSA cycle in this paper is able to be considered as an effective way to further improve exergy efficiency for heat utilization. Theoretical exergy efficiency of 4-step TSA cycle could be improved by around 20%-30% due to considerable heat of adsorbent and adsorption reactor.

5. Conclusions

A 4-step TSA cycle for CO₂ capture by using heat recovery process is evaluated based on carbon pump theory. The main parameters e.g. the minimum separation work and exergy efficiency are determined by using the characteristics of AC for detailed comparison. Unused percentage and metal part of adsorption reactor are adopted for analysing the performance in real application. Conclusions are yielded as follows:

- (1) The minimum separation work doesn't change in terms of different desorption temperatures and CO₂ partial pressures for desorption. Exergy efficiency decreases with the increase of CO₂ partial pressure for desorption. Exergy efficiency increases first then decreases with the increase of desorption temperature. The highest exergy efficiency of 4-step TSA cycle is able to reach 0.221 which could be obtained at 348 K desorption temperature and 0.03 MPa CO₂ partial pressure for desorption. Also exergy efficiency increases with the increase of CO₂ partial pressure for adsorption and the decrease of adsorption temperature. For various CO₂ partial adsorption pressures and temperatures, exergy efficiency is in the range from 0.022 to 0.22.
- (2) By using heat recovery, actual work is reduced by up to 44.5% and exergy efficiency is

improved by 76.4% in terms of different CO₂ partial pressures for desorption. Considering different desorption temperatures, actual work could be reduced by up to 41.1% and exergy efficiency could be improved by up to 67.3%. When CO₂ partial pressure for adsorption increases from 0.01 MPa to 0.02 MPa, the improvement by using heat recovery could reach up to 76%.

(3) Mass ratio has a remarkable influence on thermal performance due to the increased heat input of adsorption reactor. With the increased heat exergy input of metal part, exergy efficiency decreases with the increase of mass ratio. When mass ratio increases from 0 to 8, exergy efficiency of 4-step TSA cycle without heat recovery varies from 0.167 to 0.023, which is decreased by 86.5%. Through heat recovery, exergy efficiency could be improved from 54.3% to 84.6% when mass ratio increases from 0 to 8.

(4) Heat recovery proposed for a 4-step TSA cycle is able to be considered as an effective way to further improve exergy efficiency for heat utilization. Theoretical exergy efficiency is improved by around 20%-30%.

It is quite insightful for carbon pump theory to effectively solve “top ceiling” problem of energy efficiency for CO₂ capture, which indicates thermal performance of various post-combustion capture technologies. However, it is difficult to construct and optimize a reasonable thermal cycle only based on current carbon pump theory due to the fact that it should be a compromise between theoretical thermal analysis and real chemical manufacturing process i.e. cycle and energy efficiency are better to be separated. Try to find core concept of a certain cycle for CO₂ capture e.g. adsorption for TSA and PSA, may bring some extra inspirations, which tends to be accepted with a combination of carbon pump theory. It is demonstrated that heat recovery has a positive influence on TSA in the paper. Mass

transfer is expected to improve the performance of PSA in our future work.

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510