Comparative analysis on temperature swing adsorption cycle for carbon capture by using internal heat/mass recovery

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HIGHLIGHTS

• Performance of a 4-step TSA cycle is further explored by recovery technology.
• Unused percentage and metal part have great influence on the real performance.
• Heat recovery is conducive to TSA while mass recovery is more suitable for VSA.
• The up limit of exergy efficiencies using recovery technology could reach 40–45%.

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ABSTRACT

Due to relatively high energy consumption of absorption technology, adsorption carbon dioxide capture is gathering the momentum in recent years. This paper aims to further improve the thermal performance of a 4-step temperature swing adsorption cycle by integrating internal mass recovery and heat recovery. Exergy efficiency is evaluated by using adsorption characteristics of activated carbon and compared in terms of four different situations i.e. basic cycle, heat recovery cycle, mass recovery cycle, heat and mass recovery cycle, which could illustrate the advantages and disadvantages of different recovery technologies. Results demonstrate that heat recovery and mass recovery technologies are quite conducive to improve the up limit of cycle thermal efficiency. Under the conditions of different desorption/adsorption temperatures and pressures, exergy efficiencies using recovery technologies could be improved by up to 2.86 times when compared with that of basic cycle. Besides, in real application unused percentage of adsorption reactor and metal ratio have large influence on the cycle performance while mass recovery rate has a relatively small influence. One potential application of the proposed recovery technologies is direct air capture in building ventilation system since a largest improvement could be achieved at a low carbon dioxide concentration.

1. Introduction

According to Intergovernmental Panel on Climate Change (IPCC), global temperature is predicted to increase 1.5 °C based on the pre-industrial levels between 2030 and 2052 [1]. To control atmosphere CO2 level, one solution is switching fossil fuels into renewable sources with the improved energy efficiency. The other effective way is the use of capture, utilisation and storage (CCUS) technology [2,3]. Currently, oxygen-combustion, pre- and post-combustion capture are three technical ways for capturing CO2 from power plants. Comparably, post-combustion has a relative small effect on the power generation which is the most investigated technology [4,5]. A variety of methods e.g. cryogenic, membrane, adsorption, absorption process could achieve the post-combustion carbon capture [6,7]. Among these methods, absorption technology using amine based solution e.g. monoethanolamine (MEA) could reach a commercial scale and is currently the most mature approach for capturing CO2 from power plants [8,9]. Lots of demonstration projects could be found in the recent years [10]. Nonetheless, the main disadvantages are that MEA is corrosive and consumes a large amount of energy during the regeneration process. Also it produces other components e.g. formaldehyde and various kinds of acid that cannot be regenerated by thermal heat which will inevitability reduce the usable efficiency of the reactor [11]. Compared with liquid absorption candidates for CO2 capture, solid adsorption is always regarded as a counterpart technology that has been extensively studied in the field of thermal energy storage, refrigeration and power generation.

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Solid adsorbents generally do not pose any health hazard and they can avoid the evaporation of water in the regeneration stage which results in a relatively smaller energy consumption than that of adsorption technology [14].

Cyclic operation of adsorption CO₂ capture could be divided into adsorption and desorption steps, which form different thermal cycles. The most common adsorption cycles are pressure swing adsorption (PSA) and temperature swing adsorption (TSA). The main demarcation line relies on the treatment of desorption processes. The adsorbed gases for TSA are desorbed after adsorption steps by heating the adsorbent while the pressure of adsorbent in PSA is reduced for creating the potential for desorption. If the pressure is lower than atmosphere, vacuum pressure swing adsorption (VSA) is termed as another type of PSA [15]. Due to low grade heat utilisation, TSA is quite attractive among adsorption carbon capture technologies. Another reason is that PSA is predicted to be more costly than heating the solid material [15]. Based on carbon pump concept proposed recently, exergy efficiencies of carbon capture cycle could be evaluated for comparison. Therefore, a thermal cycle with a higher exergy efficiency reveals more potentials to reduce the energy penalty. In our previous work, analogy is used to compare adsorption refrigeration cycle with adsorption carbon capture cycle. Exergy efficiency of a 4-step TSA cycle is further improved by using internal heat recovery (IHR) [16]. It is acknowledged that heat recovery and mass recovery are independent and interdependent when considering adsorption cycles. Different recovery technologies would play different roles in regeneration heat and cycle performance. Comparably, internal mass recovery (IMR) is to recover additional mass adsorption capacities between the reactors [17]. Li et al. [18] conducted the entropy analysis on the thermodynamic cycle by using IHR and indicated the importance of the heat recovery technology. This study also indicated the potential of pressure difference which proved the significance of the IMR from another perspective [18]. Although small heat transfer happens during the mass recovery process, it doesn’t change the basic concept of IMR. IHR and IMR target different temperature and pressure potentials, which respectively reduce the regeneration heat per mass of CO₂. In the end of our recent work, a novel design was proposed for a TSA system by using internal heat and mass recovery (IHMR) tank. However, cycle performance of CO₂ capture by using IHMR had not been analysed. The core problems are not ensured i.e. whether IMR/IHMR is useful and how effective it is to adsorption carbon capture, which are quite interesting to give the answer in this paper.

In general, diverse classes of adsorbents have been identified for CO₂ capture technology, which are mainly divided into physical and chemical adsorbents according to their reaction driving force [19,20]. Chemical adsorbents usually have higher sorption capacities and relative high regeneration temperatures when compared with those characteristics of physical adsorbents [21]. The main chemical sorbents are amine-based sorbents. However, chemical adsorbents also have some drawbacks e.g. degradation caused by the reaction with oxygen and the causticity which may result in some barriers like maintenance and the causticity which may result in some barriers like maintenance. In the real application [22]. Due to the potentials of high selectivity, large sorption capacity and relatively low regeneration heat, metal-organic framework (MOF) could combine advantages of both physical and chemical adsorbents, which has set off a research boom in the past few years [23]. A comprehensive analysis of 11 types of the adsorbents has been conducted and it indicated that Mg-MOF-74 was a prospective material that could be used in TSA technology for post combustion carbon capture [24]. The main drawback is that the cost of MOF cannot be further reduced to the cheap price as other sorbents e.g. AC and zeolite. Besides, kinetics of AC and zeolite in the adsorption and desorption processes have been investigated by various research studies. Hence, their properties could be available to be used for further evaluation of different applications, which will give more general insights and inspirations when compared with those adsorbents that have higher sorption performance [25,26].
This paper aims to appraise the performance of a 4-step TSA cycle by using IMR for CO₂ capture, which has not been covered in any literature. The main novelties mainly lie in up limit exploration of cycle performance, three key parameters in real application and a potential application proposed in terms of different recovery technologies. Besides, AC is selected as the adsorbent, which is used to compare the performance with that using IHR in our previous work. Regeneration heat and exergy efficiency are then determined in terms of various adsorption/desorption temperatures and pressures. Cycle performance with IHR, IMR and IHMR will be analysed separately and compared with that of the basic cycle for further illustrating their advantages and disadvantages. The framework of this paper is illustrated as follows. The novel cycle is introduced in Section 2 where working principles of adsorption cycles are illustrated. Then methodology applied in the study is presented in Section 3. Section 4 presents the results and discussions followed by conclusions in Section 5.

2. Working principles of adsorption cycles for carbon capture

The general schematic diagram of a basic 4-step TSA cycle is shown in Fig. 1 which is depicted by using fixed reactors according to carbon pump theory based on the following assumptions [27].

(1) Temperature inside the adsorbent is uniform by considering the equilibrium performance, i.e. no temperature gradient happens in different directions. This is mainly because performance analysis of thermodynamic cycle is the main research target rather than real reaction.

(2) CO₂ is the main adsorbate in adsorbent when compared with other adsorbates e.g. N₂, water which can be neglected.

(3) CO₂ is evenly distributed in adsorber and sorbent material during each adsorption and desorption process of the TSA cycle.

A basic 4-step TSA cycle is composed of four working processes i.e. adsorption, preheating, desorption and precooling. The details of each step could refer to our previous work [16]. Thus, it is briefly illustrated according to Fig. 1 as follows:

- Step 1-2 is an adsorption process. During this process, gas mixture flows into the adsorption reactor. Then CO₂ is adsorbed by the adsorbent, and reaction heat is removed by cooling water. Theoretical adsorption process could reach point 5 but cannot achieve that in real application.

- Step 2-3 is a preheating process. Adsorption reactor is immediately heated by heating medium. Temperature of the reactor is increased but no CO₂ is desorbed.

- Step 3-4 is a desorption process. After temperature reaching T₃ at point 3, desorption process of CO₂ begins, and CO₂ with a high concentration flows out of the reactor until its temperature reaches T₄.

- Step 4-1 is a precooling process. Cooling medium is used to remove the heat from adsorption reactor. The operation conditions are resumed by starting a new 4-step TSA cycle.

Fig. 1. Schematic diagram of a 4-step TSA cycle for CO₂ capture.

Fig. 2. Clapeyron diagram of a 4-step TSA cycle for CO₂ capture.
Clapeyron schematic diagram of a basic 4-step TSA cycle is shown in Fig. 2, which is corresponding to each process in Fig. 1.

As it is mentioned in introduction, IHR and IMR have been used for improving the performance of several adsorption technologies e.g. refrigeration and power generation [13,28]. For post-combustion carbon capture, a theoretical 4-step TSA cycle with IHR between 1-2-3 and 3-4-1 process is presented in Fig. 3. In real operation, heat recovery begins when one reactor finishes adsorption at point 1, and the other reactor finishes desorption at point 3. The sensible heat of adsorber and adsorbent is then recovered. Theoretically, the temperature could reach $T_{r,i}$ i.e. the average temperature of adsorption and desorption temperature.

Considering IMR cycle, the innovative point is to utilise the large pressure difference between adsorber and desorber. The IMR could be achieved by interconnecting the adsorber and desorber after the adsorption and desorption, respectively. Then CO$_2$ will flow from desorber to adsorber for further desorption until two reactors reach the same pressure $P_{r,m}$. Then connection will be broken by closing the valve, and each reactor continues heating and cooling process as the beginning of a basic cycle. It is better to use IMR before IHR due to the relatively large pressure difference. The 4-step TSA cycle with IMR is indicated in Fig. 4 which is quite similar to that of physical adsorption refrigeration without the refrigerant side [29]. It could be observed that the cycle expands from 1-2-3-4-1 to 1-2-6-7-4-8-9-1. The best mass recovery cycle is 1-2-6-7-4-8-9-1 when processes 2-6 and 4-8 operate as isothermal processes. Thus, cycle working capacity could be further increased which results in that the desorption heat per kilogram adsorbed CO$_2$ is significantly reduced.

Four main variable parameters i.e. adsorption/desorption temperature and pressure are used to evaluate and compare thermal performance of a 4-step TSA cycle with IHR, IMR and IHMR technologies, and these temperature and pressure are also the boundary conditions for the thermal models in the next section. Adsorption/desorption temperature and pressure of CO$_2$ are adopted from 293 K to 358 K and from 0.1 bar to 0.6 bar, respectively. One representative example is selected to illustrate the advantage of IMR on the working capacity of a 4-step TSA cycle which is indicated in Fig. 5. Different from the P-T diagram of adsorption CO$_2$ capture in Fig. 4, it could be observed that reaction lines for desorption is much close to each other when compared with adsorption lines. Thus the additional capacity $\Delta q$ of IMR in the desorption process i.e. 2-6' is larger than that in the adsorption process i.e. 4-8. The smaller working capacity is then evaluated in the whole cycle. It is indicated that additional sorption capacity between point 9 and point 1 by using IMR is around two-fifth of capacity of the original cycle (capacity difference between point 9 and point 2) under the condition of 293/348 K adsorption/desorption temperature and 0.15/0.4 bar adsorption/desorption partial pressure of CO$_2$. A potential reduction of regeneration heat is expected in terms of different adsorption/desorption temperature and pressure, which will be further illustrated in the rest of the paper.

3. Analytical methodology of 4-step TSA cycles

3.1. Adsorption isotherms

The adsorption and desorption characteristics of AC adopted in this paper could refer to reference [25], Dubinin-Astakhov (D-A) Eq. (1) is applied to calculate the adsorption capacity $q$ of the 4-step TSA cycle as shown in Fig. 1 and the concerning coefficients are also obtained from the reference [25].

$$q = \left(\frac{q_0}{V_a}\right) \exp\left(-\frac{A}{E}\right)$$

(1)

where $V_a$ is the specific volume of the liquid adsorbate and $A$ is the adsorption potential which can be calculated in the Ref. [30].

Characteristics energy (E), adsorbent’s surface-structural heterogeneity factor (n), the limiting volumetric adsorbate uptake ($q_0$) and specific heat capacity ($C_p$, AC), are 4957.9 J·mol$^{-1}$, 1.24, 1.1 $\times$ $10^{-6}$ m$^3$·g$^{-1}$ and 825 Jkg$^{-1}$·K$^{-1}$, respectively.

3.2. Thermodynamic evaluation

According to the Ref. [27], thermodynamic carbon pump is defined and illustrated. Working capacity (WC) of adsorption CO$_2$ capture is expressed as following Eqs. (2) and (3), in which WC$^*$ denotes the ideal working capacity and WC denotes the real working capacity.

$$WC^* = q_1 - q_i$$

(2)

$$WC = q_2 - q_i$$

(3)

where $q_1$, $q_2$ and $q_5$ are adsorption capacity of point 1, 2 and 5 as shown in Fig. 1.

The minimum separation work ($W_{min}$) for the 4-step TSA cycle is to indicate the ease or complexity of CO$_2$ separation process. It could be calculated by Gibbs equation. Based on carbon pump theory, $W_{min}$ is only relevant to three parameters i.e. heat input temperature $T_{in}$, CO$_2$ fraction ($y_{CO2}$) and recovery rate ($R_{rec}$), which could be expressed as Eq. (4).

$$W_{min} = G(T_{in}, y_{CO2}, R_{rec})$$

(4)

Exergy efficiency is the ratio of the minimum separation work to actual work ($W_r$). Therefore, exergy efficiency of the 4-step TSA cycle is evaluated as Eq. (5), which refers to the Ref. [31].

$$\eta_{ex} = \frac{W_{min}}{W_r} = \frac{W_{min}}{W_5 + Q_h (1 - \frac{0}{\eta}) - Q_c (1 - \frac{0}{\eta})}$$

$$= \frac{W_{min}}{Q_h (1 - \frac{0}{\eta}) - Q_c (1 - \frac{0}{\eta})}$$

(5)

where $W_r$ is input work, $Q_h$ is regeneration heat, $Q_c$ is heat output of low temperature heat source, $T_1$ is low temperature of adsorption, $T_{hr}$ is high temperature of regeneration, $T_2$ is environmental temperature. Adsorption and desorption temperature are the average temperature in the reaction process. The item $W_5$ is considered to be zero due to no extra power apparatus.

Regeneration heat $Q_h$ for a 4-step TSA cycle in Eq. (5) is composed of reaction heat and sensible heat with regard to unit mass of captured CO$_2$ which could be expressed as Eq. (6).

![Fig. 3. Schematic diagram of a 4-step TSA cycle with IHR between two identical adsorption reactors.](image-url)
\[ \Delta q = \Delta q_{26} = \Delta q_{48} \]  

where the subscripts denote working state according to Fig. 4, e.g. \( \Delta q_{26} \) means the difference sorption capacity between point 4 and point 6.

In real application, the isothermal IMR cannot be achieved. Thus, the additional working capacity \( \Delta q \) could then be calculated based on Eqs. (10)–(12).

\[ (C_{p,a} + C_{p,CO_2} \Delta q_{26})(T_2 - T_1) = H_i \Delta q_{26}' \]  
\[ (C_{p,a} + C_{p,CO_2} \Delta q_{48}) (T_4 - T_6) = H_i \Delta q_{48}' \]  
\[ R_i = P_T \]  

where \( C_{p,a} \) and \( C_{p,CO_2} \) are the specific heat of the adsorbent and adsorbed CO\(_2\), \( \Delta q_{26}' \) denotes the difference sorption capacity between point 2 and point 6', \( H_i \) is the reaction heat of adsorbent.

From the equations of performance analysis, it could be found that IHR and IMR aim to improve the cycle performance from different aspects, which either decrease the numerator or reduce denominator when calculating the regeneration heat.

### 3.3. Variable factors used for flexibility analysis

Thermal performance of a 4-step TSA cycle with recovery technologies could be influenced by various factors e.g. heat and mass transfer performance, unused percentage, etc. Three main variable parameters are then adopted to further illustrate the performance in real application, which are listed as follows.

It is acknowledged that the adsorption reactor could not be efficiently used due to dead volume in the system. The unused percentage of adsorption reactor (\( \psi_{un} \)) is defined according to Eq. (13).

\[ \psi_{un} = 1 - \frac{q_5}{q_6} \]  

where \( q_1, q_2 \) and \( q_5 \) are adsorption capacities of point 1, 2 and 5 in Fig. 1.

Mass ratio between mass of adsorption reactor and adsorbent (\( \varphi_{mr} \)) is adopted as Eq. (14), which is used to evaluate its influence on IHR in real application.

\[ \varphi_{mr} = \frac{M_r}{M_a} \]  

where \( M_r \) and \( M_a \) are the mass of adsorption reactor and adsorbent, respectively.

Mass recovery coefficient (\( \varepsilon_{mr} \)) is used as the real recovered mass capacity divided by ideal recovered capacity under isothermal condition. It is used to evaluate its influence on the performance of IMR in real application, which is shown as Eq. (15).

\[ \varepsilon_{mr} = \frac{\Delta q}{\Delta q_i} \]  

where \( \Delta q \) and \( \Delta q_i \) are real and ideal additional working capacity, respectively.

### 4. Results and discussions

Theoretical performance of 4-step TSA cycles is first evaluated based on the carbon pump theory by using the characteristics of AC. Regeneration heat and exergy efficiency are two main outputs which are compared in terms of basic cycle, cycle with IHR, cycle with IMR and cycle with IHMR. Regeneration heat is defined as the specific value divided by mass of CO\(_2\) working capacity which is simplified as regeneration heat in this section. Afterwards, the unused percentage of adsorption reactor, mass ratio between adsorption reactor and adsorbent as well as mass recovery coefficient are adopted for further assessing the performance in real application.
4.1. Theoretical performance

Regeneration heat and exergy efficiency of 4-step TSA cycles are presented under the conditions of the aforementioned selected desorption/adsorption temperature and pressure which are respectively indicated in Fig. 6, Fig. 7, Fig. 8 and Fig. 9. When one parameter e.g. desorption temperature varies, others i.e. desorption temperature, adsorption temperature and pressure keep the same.

As shown in Fig. 6a, regeneration heat increases with the increase of desorption pressure due to the fact that working capacity greatly decreases with the increase of desorption pressure according to Eq. (6). The recovery technologies do have great influence on the reduction of regeneration heat. IHR could be more effective at low desorption pressure whereas the cycle with IMR shows better performance at high desorption pressure. The reasons are illustrated as follows: total working capacity is relatively large when desorption pressure is low. Additional adsorption capacity caused by IMR is relatively small when compared with total working capacity which indicates a small percentage. Thus the cycle using IMR could result in a limited reduction of regeneration heat. Comparably, when the desorption pressure increases, the ratio between additional adsorption capacity and total working capacity greatly increases which improves the effect of IMR. Due to similar temperature difference between heating and cooling source, the proportion of reduction is close at different desorption pressure. Based on Eq. (5), exergy efficiency is evaluated and shows a reverse trend in Fig. 6b. Results indicate that the highest exergy efficiency of 4-step TSA cycles with recovery technologies could reach 0.465 by using IHMR at a desorption pressure of 0.03 MPa. When the desorption pressure varies from 0.03 MPa to 0.06 MPa, exergy efficiency ranges from 0.065 to 0.0465 by using IHMR at a desorption pressure of 0.03 MPa. When the desorption pressure increases, the ratio between additional adsorption capacity and total working capacity cannot be further improved greatly.

4.2. Flexibility analysis for real applications

This subsection aims to investigate the influence of recovery technologies on thermal performance of the 4-step TSA cycles in real application. Three variables i.e. unused percentage of adsorption reactor, mass ratio between adsorption reactor and adsorbent as well as mass recovery coefficient are adopted for further illustration.

Unused percentage aims to evaluate the usage rate of adsorption reactor. Since the unused percentage usually cannot be higher than

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Fig. 6. Thermal performance of 4-step TSA cycles at different CO$_2$ partial pressures for desorption (a) regeneration heat; (b) exergy efficiency.
40% [32], percentage of 0, 10%, 20% and 30% are selected for detailed comparison and further analysis, which could refer to Fig. 10. Fig. 10a indicates regeneration heat of the cycle in terms of different unused percentages of adsorption reactor. Results reveal that regeneration heat increases sharply with the increase of the unused percentage of the reactor since the working capacity declines and the excessive sensible heat input for unused part of reactor increases. Fig. 10b shows exergy efficiency of the cycle in terms of different unused percentages, which increases with the decrease of unused percentage. When the percentage increases from 0 to 30%, exergy efficiency ranges from 0.048 to 0.38. The improvement by using IHMR is up to 2.68 times in terms of different unused percentages. It is acknowledged that the unused part of the reactor cannot be avoided since it is strongly related to reactor types, working conditions, filling methods, heat and mass transfer performance, etc. However, IHMR could improve the cycle efficiency by at least 2 times which would be more effective and prospective when unused percentage is increased.

According to Eq. (14), mass ratio is defined as the specific value between mass of sorption reactor and adsorbent. Exergy efficiency of 4-step TSA cycles in terms of different mass ratios is presented in Fig. 11. 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 input of metal part, exergy efficiency decreases with the increase of mass ratio. When mass ratio increases from 0 to 8, exergy efficiency of a 4-step TSA cycle varies from 0.37 to 0.022. One remarkable fact is that the positive influence on exergy efficiency of the
cycle is greatly reduced with the increase of mass ratio. When the mass ratio is higher than 4, IMR almost has no contribution on the improvement of exergy efficiency. This is because the high mass ratio results in the high regeneration heat input. It will significantly reduce the percentage of additional sorption capacity which makes IMR less meaningful. Under this scenario, the performance could be improved by only using the IHR. In real application, the mass ratio between adsorbent and adsorption reactor could be within 1–2 for post-combustion CCS system when compared with other adsorption applications e.g. adsorption cogeneration whose mass ratio is usually higher than 3 [33]. When the mass ratio is able to reach 2, the improvement of exergy efficiency by using IMR, IHR and IHMR could reach about 19.1%, 84.9% and 96.2%, respectively. It will become more desirable when the mass ratio is less than 2.

Fig. 12 indicates exergy efficiency of 4-step TSA cycles in terms of different mass recovery coefficients which could be affected by various factors e.g. pipe shape, valve type, recovery time, etc. It could be observed that mass recovery coefficient has no influence on the exergy efficiency of the cycle using IHR since no pressure potential could be recovered. When mass recovery coefficient varies from 0.5 to 1, exergy efficiencies of the cycle using IMR and IHMR increase from 0.198 to 0.229 and 0.328 to 0.382. Within this range from 0.5 to 1, the largest increment is no more than 20% which reveals that the improvement of mass recovery coefficient has a small influence on exergy efficiency of the cycle using IMR. Thus, IMR should be applied for a 4-step TSA cycle in real application. However, there is no need to further optimise IMR by increasing the cost to use very high-quality valves and pipes though the suggested mass recovery coefficient is from 0.8 to 0.9 according to the common adsorption refrigeration mass recovery cycle [34].

4.3. Further comparison and insight

In order to further illustrate different roles of recovery methods, exergy efficiencies of different post-combustion carbon capture technologies are first presented and different adsorption cycles are compared [27,35]. Fig. 13 indicates exergy efficiencies of different post-combustion CCS technologies when CO₂ concentrations of flue gas are between 10% and 15%. It reveals that different technologies have their up limits of exergy efficiencies for CO₂ capture. For cryogenics and other technologies, the efficiencies are generally lower than 10%. Sorption technologies e.g. adsorption and absorption are usually lower than 25% without using IHR/IMR. Exergy efficiency of membrane carbon capture technology could be a bit higher than 25% which is mainly determined by the materials. Fig. 14 shows exergy efficiencies of selected adsorption cycles i.e. TSA, VSA, pressure-temperature swing adsorption (PTSA) and electric swing adsorption (ESA) in terms of different recovery technologies when CO₂ concentrations range from 5% to 20%. The results of the basic cycle refer to the Ref. [36]. It can be observed that IHR is quite conducive to TSA and PTSA since the external heat is used for the desorption process of materials. VSA can only...
adopt IMR for performance improvement. No related recovery technology could be applied for improving the efficiency of ESA since it aims to improve other performance e.g. fast desorption rate. It is worth noting that the upper limits of exergy efficiencies of the selected adsorption cycles using IHMR could reach between 40 and 45%.

Table 1 comprehensively compares the recovery technologies for different adsorption CCS methods in terms of cycle candidate, more suitable condition, reactor, and improvement of exergy efficiency. It is demonstrated that IHR is more suitable for high desorption temperature and the improvement of upper limit could reach at least 70% due to the large recovered heat. Comparably, IMR is better to be applied to the situation at low adsorption pressure. This is mainly because working capacity becomes much lower when adsorption pressure is low. Thus the upper limit of exergy efficiency could be increased at least 24% when compared with that of basic cycle. The cost of the recovery technologies are mainly determined by the design for retrofitting the original systems [37]. Considering IHR, it lies in more heat exchangers required for recovering the sensible heat. Comparably, the additional cost of IMR depends on the valves and pipelines for adjusting the pressure difference.

Based on above characteristics of aforementioned recovery approaches for post-combustion carbon capture technologies, a potential target application is suggested in Fig. 15. That is direct air capture (DAC) with PTSA from places with high CO2 intensity e.g. office building, hospital, farms in which CO2 concentration is usually more than 500 ppm [38]. Adsorption unit is combined with the heat and mass recovery tank, which will be integrated with central air conditioning/ventilation system. Thus, the largest improvement could be achieved by using IHMR due to a relative low CO2 concentration when compared with other sources e.g. power plant, iron and steel. The captured CO2 could then be used for the roof greenhouse, factory, soda industry, etc.

5. Conclusions

4-step temperature swing adsorption cycles for CO2 capture by using internal heat recovery, internal mass recovery as well as internal heat and mass recovery are evaluated based on carbon pump theory. The main parameters e.g. regeneration heat and exergy efficiency are determined based on characteristics of activated carbon. Unused percentage, mass ratio between adsorption reactor and adsorbent and mass recovery coefficient are adopted for analysing the performance in real application. Conclusions are yielded as follows:

(1) The regeneration heat increases with the increase of desorption pressure and adsorption temperature while it increases with the decrease of desorption temperature and adsorption pressure. Exergy efficiency shows a reverse trend of regeneration heat. Recovery technologies have great influence on reducing regeneration heat for improving exergy efficiency. Through various recovery technologies, the highest exergy efficiency of 4-step temperature swing adsorption cycles could reach 0.465 at different desorption/adsorption temperature and pressure, which improves the efficiency up to 3.5 times compared with the performance of basic

![Fig. 13. Exergy efficiencies of various post-combustion CCS technologies [27,35].](image1)

![Fig. 14. Exergy efficiencies of the selected adsorption cycles in terms of different recovery technologies [36].](image2)

![Fig. 15. Potential target application by using IHMR technology.](image3)

| Item | Applied cycle | More suitable conditions | improvement | Additional cost |
|------|--------------|--------------------------|-------------|----------------|
| IHR  | TSA, PTSA    | High desorption temperature | At least 70% | Heat exchanger  |
| IMR  | TSA, VSA, PTSA | Low adsorption pressure     | At least 24% | Pipeline       |
| IHMR | TSA, VSA, PTSA | No preference              | At least 24% | Above two      |
cycle.

(2) Unused percentage of adsorption reactor and metal ratio have large influence on the performance of adsorption cycles while mass recovery coefficient has a relatively small influence. When the unused percentage increases from 0 to 30%, exergy efficiency ranges from 0.048 to 0.38. IHMR could improve the cycle efficiency by at least 2 times which will be more effective when unused percentage is increased. Besides, when mass ratio increases from 0 to 8, exergy efficiency of the cycle varies from 0.37 to 0.022. When mass ratio is higher than 4, internal mass recovery almost has no influence on the improvement of exergy efficiency. When mass recovery coefficient varies from 0.5 to 1, the largest increment is no more than 20%.

(3) Internal mass recovery is quite conducive to temperature swing adsorption and pressure-temperature swing adsorption while vacuum swing adsorption can only adopt internal mass recovery for performance improvement. The up limits of exergy efficiencies of adsorption cycles using internal heat and mass recovery could reach between 40 and 45%. Internal heat recovery is more suitable for high desorption temperature and its up limit of exergy efficiency could be improved by at least 70%. Comparably, internal mass recovery is better to be applied to the situation at low adsorption pressure with an improvement of at least 24%.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] I.M. Saeed, P. Alaba, S.A. Mazari, W.J. Basirun, V.S. Lee, N. Sahfar, Opportunities and challenges in the development of monoethanolamine and its blends for post-combustion CO2 capture, Int. J. Greenhouse Gas Control 79 (2018) 212–233.
[2] L. Zhao, R. Zhao, S. Deng, Y. Tan, Y. Liu, Integrating solar Organic Rankine Cycle into a coal-fired power plant with amine-based chemical absorption for CO2 capture, Int. J. Greenhouse Gas Control 31 (2014) 77–86.
[3] F. Su, C. Lu, CO2 capture from gas stream by zeolite 13X using a dual-column temperature/vacuum swing adsorption, Energy Environ. Sci. 5 (10) (2012) 9021–9027.
[4] D.P. Hanak, S. Michalkis, V. Manovic, From post-combustion carbon capture to sorption-enhanced hydrogen production: A state-of-the-art review of carbonate looping process feasibility, Energy Convers. Manage. 177 (2018) 428–452.
[5] A. Qafzhi, M. Sharma, F. Pavarhe, R. Khalilpour, A. Abbas, Flexible dynamic operation of solar-integrated power plant with solvent based post-combustion carbon capture (PCC) process, Energy Convers. Manage. 99 (2015) 7–19.
[6] M.K. Mondal, H.K. Balsora, P. Vashishey, Progress and trends in CO2 capture/separation technologies: A review, Energy 46 (1) (2012) 431–441.
[7] S. Baik, H. Zhang, Y.K. Kim, D. Harbottle, J.W. Lee, Enhanced adsorption capacity and selectivity towards tritium ions in aqueous systems by saponification of CO2 derived porous carbon, RSC Adv. 7 (86) (2017) 54546–54553.
[8] P. Luis, Use of monoethanolamine (MEA) for CO2 capture in a global scenario: Consequences and alternatives, Desalination 380 (2016) 93–99.
[9] A. González Díaz, E. Sánchez Fernández, J. Gibris, M. Lucquiaud, Sequential supplementary firing in natural gas combined cycle with carbon capture: A technology option for Mexico for low-carbon electricity generation and CO2 enhanced oil recovery, Int. J. Greenhouse Gas Control 51 (2016) 330–345.
[10] R. Idré, T. Supap, H. Shi, D. Gelowitz, M. Ball, C. Campbell, et al., Practical experience in post-combustion CO2 capture using reactive solvents in large pilot and demonstration plants, Int. J. Greenhouse Gas Control 40 (2015) 6–25.
[11] G.S. Goff, G.T. Rochelle, Monoethanolamine degradation: O2 mass transfer effects under CO2 capture conditions, Ind. Eng. Chem. Res. 43 (20) (2004) 6400–6408.
[12] L. Jiang, L. Wang, R. Wang, F. Zhu, Y. Lu, A.P. Roskilly, Experimental investigation on an innovative resorption system for energy storage and upgrade, Energy Convers. Manage. 138 (2017) 651–658.
[13] L. Jiang, A.P. Roskilly, R.Z. Wang, L.W. Wang, Analysis on innovative resorption cycle for power and refrigeration cogeneration, Appl. Energy 218 (2018) 10–21.
[14] G. Schirme, F. Dietrich, J. Fuchs, T. Proll, H. Hofbauer, A multi-stage fluidized bed system for continuous CO2 capture by means of temperature swing adsorption – First results from bench scale experiments, Powder Technol. 316 (2017) 519–527.
[15] R. Zhao, L. Zhao, S. Deng, C. Song, J. He, Y. Zhao, et al., A comparative study on CO2 capture performance of vacuum-pressure swing adsorption and pressure-temperature swing adsorption based on carbon pump cycle, Energy. 137 (2017) 495–509.
[16] L. Jiang, A.P. Roskilly, R.Z. Wang, Performance exploration of temperature swing adsorption technology for carbon dioxide capture, Energy Convers. Manage. 165 (2018) 396–404.
[17] M.Z.I. Khan, R.B. Saha, K.C.A. Alam, A. Aksiuwa, T. Kashiwagi, Study on solar/waste heat driven multi-bed adsorption chiller with mass recovery, Renewable Energy 32 (3) (2007) 365–381.
[18] S. Li, S. Deng, R. Zhao, L. Zhao, W. Xu, X. Yuan, et al., Entropy analysis on energy consumption process and improvement method of temperature/vacuum swing adsorption (TVSA) cycle, Energy. 179 (2019) 876–889.
[19] B.B. Saha, S. Jirbi, S. Koyama, I.I. El-Sharkawy, Carbon dioxide adsorption isotherms on activated carbons, J. Chem. Eng. Data 56 (5) (2011) 1974–1981.
[20] Y.J. Zhao, L.W. Wang, R.Z. Wang, K.Q. Ma, L. Jiang, Study on consolidated activated carbon: Choice of optimal adsorbent for recycling application, Int. J. Heat Mass Transfer. 67 (Supplement C) (2013) 867–876.
[21] C. Chen, S. Zhang, K.H. Row, W.-S. Ahn, Amine-silica composites for CO2 capture: A short review, J. Energy Chem. 26 (5) (2017) 866–880.
[22] W. Zhao, H. Liu, Y. Sun, J. Cai, Synthetic C3 Sun, C.E. Snape, Parametric study on the regeneration heat requirement of an amine-based solid adsorbent process for post-combustion carbon capture, Appl. Energy 168 (2016) 394–405.
[23] W. Zhang, X. Liu, Q. Zhao, J. He, L. Zhao, Carbon pump: Fundamental theory and applications, Energy. 119 (2017) 1131–1143.
[24] L. Jiang, R.Z. Wang, L.W. Wang, A.P. Roskilly, Investigation on an innovative resorption system for seasonal thermal energy storage, Energy Convers. Manage. 149 (2017) 129–139.
[25] W. Wang, T.F. Qu, R.Z. Wang, Influence of degree of mass recovery and heat regeneration on adsorption refrigeration cycles, Energy Convers. Manage. 43 (5) (2002) 733–741.
[26] J. Xiao, R. Peng, D. Cossement, P. Bénard, R. Chahine, CFD model for charge and discharge cycle of adsorption heat energy storage on activated carbon, Int. J. Hydrogen Energy 38 (3) (2013) 1439–1447.
[27] B. Li, Y. Duan, D. Luebke, B. Morreale, Advances in CO2 capture technology: A patent review, Appl. Energy 102 (2013) 1439–1447.
[28] B. Li, Y. Duan, D. Luebke, B. Morreale, Advances in CO2 capture technology: A patent review, Appl. Energy 102 (2013) 1439–1447.
[29] R. Zhao, S. Deng, Y. Liu, Q. Zhao, J. He, L. Zhao, Carbon pump: Fundamental theory and applications, Energy. 119 (2017) 1131–1143.
[30] L. Jiang, R.Z. Wang, L.W. Wang, A.P. Roskilly, Investigation on an innovative resorption system for seasonal thermal energy storage, Energy Convers. Manage. 149 (2017) 129–139.
[31] L. Wang, T.F. Qu, R.Z. Wang, Influence of degree of mass recovery and heat regeneration on adsorption refrigeration cycles, Energy Convers. Manage. 43 (5) (2002) 733–741.
[32] J. Xiao, R. Peng, D. Cossement, P. Bénard, R. Chahine, CFD model for charge and discharge cycle of adsorption heat energy storage on activated carbon, Int. J. Hydrogen Energy 38 (3) (2013) 1439–1447.
[33] B. Li, Y. Duan, D. Luebke, B. Morreale, Advances in CO2 capture technology: A patent review, Appl. Energy 102 (2013) 1439–1447.
[34] R. Zhao, S. Deng, Y. Liu, Q. Zhao, J. He, L. Zhao, Carbon pump: Fundamental theory and applications, Energy. 119 (2017) 1131–1143.
[35] L. Jiang, R.Z. Wang, L.W. Wang, A.P. Roskilly, Investigation on an innovative resorption system for seasonal thermal energy storage, Energy Convers. Manage. 149 (2017) 129–139.
[36] W. Wang, T.F. Qu, R.Z. Wang, Influence of degree of mass recovery and heat regeneration on adsorption refrigeration cycles, Energy Convers. Manage. 43 (5) (2002) 733–741.