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Comparative analysis of thermodynamic theoretical models for energy consumption of CO_2 capture*

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Abstract: CO_2 capture is considered an effective technology to control the CO_2 level in the atmosphere, but its development has been restricted due to its high energy requirement during CO_2 concentration. Theoretical thermodynamic models have been used not only to predict energy consumption, but also to elucidate the energy conversion mechanism. However, the existing theoretical models have been applied without a clear consideration of boundaries, conditions, and limitations in thermodynamic images. Consequently, the results from such theoretical models can lead to a misunderstanding of the energy conversion mechanism during CO_2 capture. A comparative analysis of three theoretical thermodynamic models, namely the mixture gas separation (MGS), carbon pump (CP), and thermodynamic carbon pump (TCP) models, was presented in this paper. The characteristics of these models for determining the energy consumption of CO_2 capture were clarified and compared in relation to their practical application. The idealization levels of these models were demonstrated through comparison of theoretical estimates of the energy required for CO_2 concentration. The correctness and convenience of the CP model were proved through a comparison between the CP and MGS models. The TCP model proposed in this study was proved to approach the ideal status more closely than the CP model. Finally, an application of the TCP model was presented through a case study on direct capture of CO_2 from the air (DAC).

Key words: CO_2 capture; Energy consumption; Theoretical model; Carbon pump
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1 Introduction

The control of the CO_2 level in the atmosphere is urgent according to the 1.5 °C special report of the Intergovernmental Panel on Climate Change (IPCC) (IPCC, 2018). Thus, the development of CO_2 capture technology has attracted much attention in the past 20 years (Ben-Mansour et al., 2016; Li et al., 2018). How to obtain clear and accurate theoretical values of energy consumption for CO_2 capture is a major concern in this research field, as energy consumption is still the main contributor to cost (GCCSI, 2018).

CO_2 capture is currently regarded as an energy-intensive technology (EIT) due to its high energy consumption. Even CO_2 absorption technology, regarded as the most near-commercial technology in the CO_2 capture field, consumes nearly 3–4 GJ of thermal

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energy per ton of CO_2 captured (Jassim and Rochelle, 2006). On the other hand, the application of EIT would make it more difficult to achieve decarbonization of the current industrial system.

Three kinds of models have been applied in the CO_2 capture field as tools for analyzing energy consumption: mixture gas separation (MGS) (House et al., 2009), process engineering (Zhao B et al., 2017), and life cycle assessment (LCA) (Odeh and Cockerill, 2008) models (Fig. 1). However, among these three tools, only the MGS model can be regarded as a theoretical thermodynamic model, based on the first and second laws of thermodynamics.

An understanding of the basis of energy consumption is necessary, including the energy conversion mechanism. Classical concepts of thermodynamics, such as enthalpy and entropy, have been applied to CO_2 capture research. For energy-saving research, a theoretical thermodynamic model needs to be established that can be applied in the CO_2 capture field for the exploration of energy conversion mechanics.

The fundamental equation of classical thermodynamics (Eq. (1)) was defined by Gibbs who considered the exchange between the heat and mechanical work in a cycle ($\mathrm{d}u=0$) (Zhao et al., 2017a). As for the fundamental equation of thermodynamics of the adsorption system, which could be regarded as an open system, the differential internal energy u could be calculated as shown in Eq. (2). Hence, the variation of the Gibbs free energy ($\mu \mathrm{d}n$) should be considered here as one form of energy.

$$\mathrm{d}u = T\mathrm{d}s - P\mathrm{d}v, \tag{1}$$

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_{i=1}^{n} \mu_i \mathrm{d}n_i, \tag{2}$$

where T is the temperature, s is the specific entropy, P is the pressure, v is the specific volume, U is the total internal energy, S is the total entropy, V is the total volume, n is the quantity, and μ_i is the chemical potential of the component i.

The carbon pump (CP) model was proposed by Zhao et al. (2017a) to obtain the ideal energy consumed by CO_2 capture with the calculation of Gibbs free energy variation of gas separation. Theoretical analysis has been conducted to compare the second-law thermodynamic efficiency of several representative applications, e.g. temperature swing adsorption (TSA) (Zhao et al., 2017d; Jiang et al., 2018) and pressure swing adsorption (PSA) (Zhao et al., 2017b, 2017c). However, the relative performance of the CP and MGS models when applied to engineering projects is still not clear. Therefore, the CP model is chosen as a comparative model in this study.

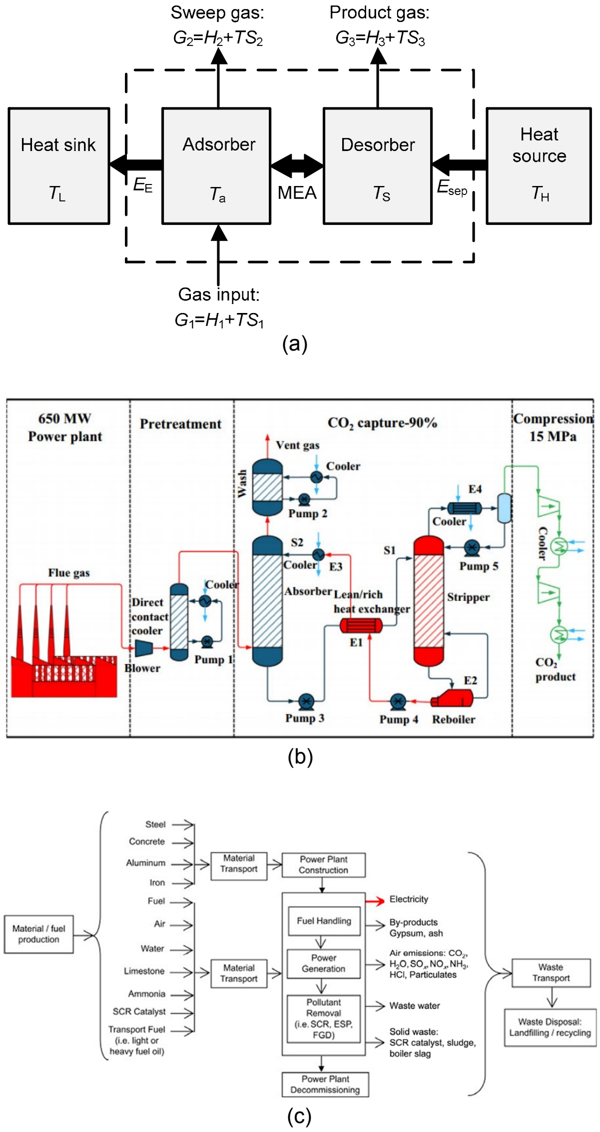

Fig. 1 Sketch of three research tools: (a) MGS model; (b) process engineering model; (c) LCA model

G is the Gibbs free energy; H is the enthalpy; T_L is the low temperature; T_a is the adsorption temperature; T_S is the desorption temperature; T_H is the high temperature; E_E is the exothermic energy; E_{sep} is the separation energy; MEA indicates monoethanolamine; SCR is the selective catalytic reduction; ESP is the electrostatic precipitator; FGD is the flue gas desulfurization. Fig. 1b is reprinted from (Zhao B et al., 2017), Copyright 2017, with permission from Elsevier. Fig. 1c is reprinted from (Odeh and Cockerill, 2008), Copyright 2008, with permission from Elsevier

The thermodynamic carbon pump (TCP) model is introduced with an in-depth description of the CP model in this study. As the TCP model can be considered a thermodynamic theoretical model for ideal energy-consumption of CO_2 capture, the Gibbs free energy variation was calculated in a more ideal scenario. How the TCP model works is illustrated in Section 3.3, in which the minimum ideal energy consumption w_{ideal}' in direct capture of CO_2 from the air (DAC) is chosen as a case study.

Three kinds of thermodynamic theoretical models for evaluation of energy consumption of CO_2 capture technology are compared in this study: the MGS, CP, and TCP models. The correctness and convenience of the CP model is proved by comparison with the MGS model, and the essence of energy conversion in CO_2 capture technology is clarified in the thermodynamic aspect with the application of the CP model. Then a TCP model is proposed in which the carbon source and sink are assumed to have infinite mass capacity. The TCP model is then compared with the CP model and is proved to be more ideal. Finally, the potential application of the TCP model was researched with a case study, which proved the possibility of realizing a cross-technology comparison through the use of classical thermodynamic indicators. Thus, the integration of a thermodynamic theoretical framework into CO_2 capture was explored in this study through the comparative analysis of theoretical thermodynamic models. The framework is intended to be used to clarify the energy conversion mechanism of CO_2 capture technology. The energy-saving potential of a specific case, such as DAC, is also discussed.

2 Thermodynamic theoretical models and methods

2.1 MGS model

The MGS model is a lumped model which has been widely applied in the analysis of energy consumption during gas separation (Lively and Realff, 2016). Such a model, which has been described in textbook (Wilcox, 2012), has been used to estimate the minimum work required to separate CO_2 from a mixture of gases.

The usual situation in CO_2 capture technology is depicted in Fig. 2, in which the product gas B with high CO_2 concentration is separated from the feed gas A with low CO_2 concentration, while the sweep gas C with a subtle CO_2 concentration (within a range of 0.03%–0.05% in volume to fit the emission standard) remains.

With the application of the MGS model, the minimum separation work W_{min} has been defined and calculated by (Wilcox, 2012)

$$\begin{aligned} W_{\min} &= \Delta G_B + \Delta G_C - \Delta G_A \\ &= RT\left[N_B\varphi_B \ln\varphi_B + N_B(1-\varphi_B)\ln(1-\varphi_B)\right] \\ &\quad + RT\left[N_C\varphi_C \ln\varphi_C + N_C(1-\varphi_C)\ln(1-\varphi_C)\right] \\ &\quad - RT\left[N_A\varphi_A \ln\varphi_A + N_A(1-\varphi_A)\ln(1-\varphi_A)\right], \end{aligned} \tag{3}$$

where ΔG is the variation of Gibbs free energy, R is the gas constant, N is the amount of mixing gas in moles, and φ is the CO_2 concentration in the mixing gas. Subscripts A, B, and C indicate gas A, gas B, and gas C, respectively.

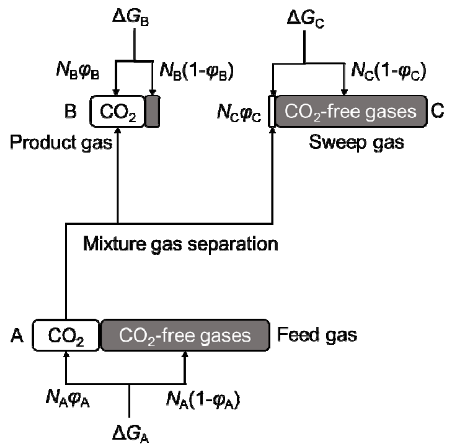

Fig. 2 A schematic diagram of the MGS model

As in the case described by Wilcox (2012), W_{min} has been applied to evaluate the energy consumption of CO_2 capture technology. However, the CO_2 capture rate ϕ, which is hard to obtain in practical systems, is required in the calculation of such an evaluation indicator:

$$w_{\min} = W_{\min} / (\phi N_A \varphi_A), \tag{4}$$

where w_{min} is the minimum separation work required to obtain one unit mole of CO_2.

Clearly, the MGS model is applicable to the analysis of the energy consumption of CO_2 capture technology, and is based primarily on the law of mass conservation, but it lacks an in-depth exploration of the energy conversion rule.

2.2 CP model

The CP model proposed by Zhao et al. (2017a) was focused primarily on the energy-efficiency of different CO_2 capture technologies. The definition and theoretical formula of the CP model are re-organized in this section, to clarify the thermodynamic aspects of such a model.

2.2.1 Definition

A heat pump has been defined in a thermodynamic field, and operates to create or maintain a temperature gradient. Hence, the concept of a "pump" is appropriate for CO_2 capture systems, which create or maintain a CO_2 concentration gradient in reverse to the direction of spontaneous diffusion. Using the heat pump as a reference concept, a CP, which achieves the enrichment of CO_2 from a carbon source to a carbon sink, is defined as shown in Table 1.

Table 1 Comparison between the CP and heat pump

Feature	Heat pump	CP
Potential indicator	Temperature	Chemical potential
Source	Ambient air	Flue gas
Sink	Indoor air	Storage unit
Drive	Heat/Power	Heat/Power
Function	Heat transfer	CO_2 concentration
Direction	Source → Sink	Source → Sink
Typical technology	Vapor-compression, absorption	Absorption, adsorption

The definition of the CP model can also be illustrated inside a thermodynamic axiomatic framework. Recalling Eq. (5), the energy conservation equation of a fixed quality system not only clarifies the conversion mechanism among various energy forms, but also reflects the conjugation between extensive and intensity parameters:

$$\mathrm{d}U = \delta Q - \delta W. \tag{5}$$

Consequently, the variation of heat Q depends only on the variation of work W when no internal energy U varies, and the variation of work can be considered as the driving force of the heat transferred in the heat pump (Fig. 3).

Similarly, the CP model follows the same research track in classical thermodynamics and is supported by complete conservation formulas, in which the variation of Gibbs free energy ΔG in a mixture depends on the variation in both the heat Q and the work W:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_{i=1}^{r} \mu_i \mathrm{d}N_i, \tag{6}$$

where r is the number of component.

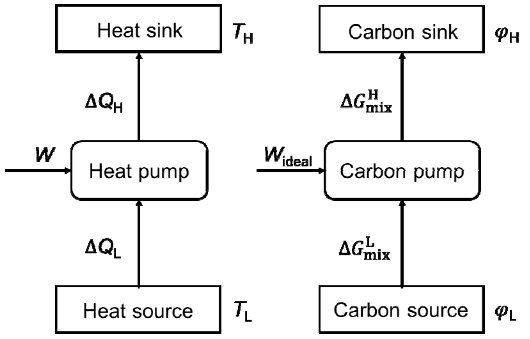

Fig. 3 A schematic diagram of the comparison between a heat pump and a carbon pump (subscripts H and L indicate the high and low CO_2 concentration sides, respectively)

As shown in Fig. 3, the definition of ideal energy consumption W_{ideal} is similar to the work input in the concept of the heat pump. Considering that the mass transfer of a specified gas (CO_2) occurs in the carbon pump, the variation of heat in the heat pump was expanded to the variation of Gibbs free energy to express the effect of mass enrichment from a carbon source with a low CO_2 concentration φ_L to a carbon sink with a high CO_2 concentration φ_H. Specifically, the sweep gas with a CO_2 concentration φ_{amb} at least lower than the environmental concentration (within a range of 0.03%–0.05% in volume) is also considered in the carbon sink, which was assumed to be 0.04% in this study.

2.2.2 Theoretical model

A CP works between a carbon sink and a source, and CO_2 enrichment is achieved by work input. The research on this process could be reinforced by the development of a theoretical model which, with suitable assumptions, could be applied in theoretical analysis as in the heat pump model. The thermodynamic theories applied in the CP model were as follows:

1. The CO_2 enrichment process is assumed to be reversible under the conditions of constant pressure and temperature.

2. The variation of Gibbs free energy is given by Eq. (7) (Turns, 2006), in which the chemical reaction is not considered:

$$\mathrm{d}G = \sum_{i=1}^{r} \mu_i \mathrm{d}N_i. \tag{7}$$

3. The gas mixtures at pressure P_0 are assumed to be an ideal gas, and the free energy of mixing of N mol of two-component gas (mixing of CO_2 and CO_2-free gas) is shown as (Haynes, 2011)

$$\Delta G_{\text{mix}} = NRT \times \left(\frac{P_{CO_2}}{P_0} \ln\left(\frac{P_{CO_2}}{P_0}\right) + \frac{P_0 - P_{CO_2}}{P_0} \ln\left(\frac{P_0 - P_{CO_2}}{P_0}\right) \right), \tag{8}$$

where P_{CO_2} is the partial pressure of CO_2 in a mixing gas, and the equation could be understood as an isothermal compression of the two components (CO_2 and CO_2-free components) of the mixing gas with hypothetical pistons respectively, into the total pressure of the mixing gas P_0.

With the above assumptions, the ideal energy consumption of the CO_2 capture technology could be simplified as

$$W_{\text{ideal}} = \Delta G_{\text{mix}}^{\text{H}} - \Delta G_{\text{mix}}^{\text{L}}, \tag{9}$$

where W_{ideal} is the ideal energy consumption required to achieve the enrichment of CO_2, $\Delta G_{\text{mix}}^{\text{L}}$ and $\Delta G_{\text{mix}}^{\text{H}}$ are the free energy of mixing of N mol of mixing gas in a carbon source and sink, respectively.

Thus, the ideal energy consumption which is based on the law of conservation of mass can be obtained as an ideal work input, given by

$$W_{\text{ideal}} = \Delta G_{\text{mix}}^{\text{H}} - \Delta G_{\text{mix}}^{\text{L}} = \Delta G_{\text{mix,B}} + \Delta G_{\text{mix,C}} - \Delta G_{\text{mix,A}}, \tag{10}$$

where A represents the flue gas, B represents the CO_2 product gas, and C represents the CO_2-free gases, such as N_2 and SO_2, in the carbon source and sink, which are assumed to be fully premixed.

Hence, Eq. (8) can be substituted into Eq. (10), and the ideal energy consumption W_{ideal}, which is the function of the concentration of CO_2 in the carbon source and sink, can be obtained as shown in Eq. (11), in which N_{H} and N_{L} are the amounts of feed gas and product gas in moles, respectively:

$$\begin{aligned} W_{\text{ideal}} = {} & RT\{N_{\text{H}}\varphi_{\text{H}} \ln\varphi_{\text{H}} \\ & + (N_{\text{L}}\varphi_{\text{L}} - N_{\text{H}}\varphi_{\text{H}}) \ln[(N_{\text{L}}\varphi_{\text{L}} - N_{\text{H}}\varphi_{\text{H}})/(N_{\text{L}} - N_{\text{H}})] \\ & + N_{\text{H}}(1-\varphi_{\text{H}})\ln(1-\varphi_{\text{H}}) \\ & + [N_{\text{L}}(1-\varphi_{\text{L}}) - N_{\text{H}}(1-\varphi_{\text{H}})] \\ & \times \ln[N_{\text{L}}(1-\varphi_{\text{L}}) - N_{\text{H}}(1-\varphi_{\text{H}})]/(N_{\text{L}} - N_{\text{H}})\} \\ & - RT[N_{\text{L}}\varphi_{\text{L}} \ln\varphi_{\text{L}} + N_{\text{L}}(1-\varphi_{\text{L}})\ln(1-\varphi_{\text{L}})]. \end{aligned} \tag{11}$$

In practical applications, the differential molar ideal energy consumption w_{ideal} (as shown in Eq. (12)) is defined to calculate the energy consumption per unit mole of CO_2 separated, which can be applied to evaluate the level of energy consumption among different technologies:

$$\begin{aligned} w_{\text{ideal}} & = \frac{W_{\text{ideal}}}{N_{\text{H,CO}_2}} \\ & = \{RT[(\varphi_{\text{L}} - \varphi_{\text{amb}})\varphi_{\text{H}} \ln\varphi_{\text{H}} \\ & \quad + (\varphi_{\text{H}} - \varphi_{\text{L}})\varphi_{\text{amb}} \ln\varphi_{\text{amb}} \\ & \quad + (\varphi_{\text{L}} - \varphi_{\text{amb}})(1-\varphi_{\text{H}})\ln(1-\varphi_{\text{H}}) \\ & \quad + (\varphi_{\text{H}} - \varphi_{\text{L}})(1-\varphi_{\text{amb}})\ln(1-\varphi_{\text{amb}})] \\ & \quad - RT[(\varphi_{\text{H}} - \varphi_{\text{amb}})\varphi_{\text{L}} \ln\varphi_{\text{L}} \\ & \quad + (\varphi_{\text{H}} - \varphi_{\text{amb}})(1-\varphi_{\text{L}})\ln(1-\varphi_{\text{L}})]\} / \varphi_{\text{H}} \\ & = f(T, \varphi_{\text{H}}, \varphi_{\text{L}}). \end{aligned} \tag{12}$$

Thus, a unified mathematical formula for evaluation of CO_2 capture technologies was established in which, based on the concept of a heat pump applied in heating supply engineering, the unified indicator represents the specialized physical phenomenon of all the CO_2 capture technologies. The ideal energy consumption defined could be applied as a classical thermodynamic indicator to accomplish interdisciplinary comparisons.

2.3 TCP model

The proposed TCP model comes from an in-depth understanding of the CP model and provides a more ideal extended state. Considering that the temperatures of the heat source and sink stay constant in a heat pump system in which it is assumed that the heat is infinite, the assumptions of the carbon source and sink in the CP model are not ideal enough.

Thus, in the TCP model the carbon source and sink are treated as having infinite mass capacity, that is, the enrichment of CO_2 in CO_2 capture technology is from an unlimited supply of the feed gas (Fig. 4). Such work was not a simple idealized assumption of the carbon source and sink, but also involved the elimination of irreversibility in the gas mixing process. Such irreversibility could be treated as an analogy of the irreversibility in a non-isothermal heat transfer process, which should be eliminated in a "Carnot cycle".

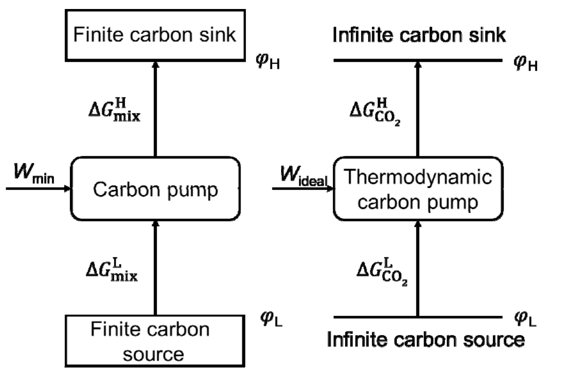

Fig. 4 A schematic diagram of the comparison between the CP and TCP models

Considering that the energy balance and entropy balance of CO_2 capture technology has been stated in the CP model, the ideal minimum energy consumption w_{ideal}' could be obtained as shown in Eq. (13) with the assumption that the fraction of CO_2 recovered is infinitesimally small, and the mass transfer of CO_2 between the carbon sink and source would not affect the free energy of the mixing gas on these two sides.

$$w'_{ideal} = \frac{\Delta G^H_{CO_2} - \Delta G^L_{CO_2}}{N_{H,CO_2}} = RT\ln\left(\frac{\varphi_H}{\varphi_L}\right). \quad (13)$$

Although the current CP model is based on the concept of conservation in thermodynamics, it cannot approach the classical analysis framework of the concept of equilibrium in thermodynamics. The TCP model could be treated as an update of the CP model, providing a quantified pathway from real to ideal status for CO_2 capture technology. The preliminary application of the TCP model is illustrated in Section 3.3 and will be discussed further in future work.

We conclude that the principles of the CP and TCP models are the same (Fig. 4), as the Gibbs free energy variation between the carbon source and sink is driven by work input. But with more assumptions added in the carbon source and sink, the irreversibility of mass transfer, which could be analogous to heat transfer in a heat pump, is eliminated.

3 Comparative study

3.1 Case I: comparative analysis of the MGS and CP models

Wilcox (2012) applied the MGS model to calculate the minimum separation work of CO_2 capture technology in an engineering project. The ideal energy consumption calculated by the CP model in the same conditions would prove the correctness and convenience of such a model.

In this case, the components of flue gas in a 500-MW coal-combustion plant include 4 kmol/s CO_2, 5 kmol/s H_2O, 1 kmol/s O_2, and 20 kmol/s N_2. As for technical indicators of this CO_2 capture project, the CO_2 capture rate should be at least 90% and the purity of product gas 98% (at a temperature of 45 °C). The known conditions are listed in Table 2.

Taking into account Eq. (10), the ideal energy consumption could be calculated as 24 756 kJ/s (6.88 kJ/mol). The application of the MGS model has been represented by Wilcox (2012) and the function is expressed as

$$\begin{aligned} W_{min} &= \Delta G_2 + \Delta G_3 - \Delta G_1 \\ &= 8.315\times 318.15\times[3.6\times\ln(0.98) \\ &\quad + 0.07\times\ln(0.02) + 0.4\times\ln(0.015) \\ &\quad + 25.93\times\ln(0.985) - 4\times\ln(0.13) \\ &\quad - 26\times\ln(0.87)] \\ &= 24756\ (\text{kJ/s}), \end{aligned} \quad (14)$$

$$w_{min} = \frac{W_{min}}{N_2\varphi_2} = \frac{24756}{3.6\times 1000} = 6.88\ (\text{kJ/mol}). \quad (15)$$

The results show that the minimum separation work calculated by the MGS model is equal to the ideal energy consumption calculated by the CP model, which indicates the correctness of the CP model (Fig. 5).

As shown in Table 2, the required parameters of the CP model include (1) the reaction temperature, (2) the CO_2 concentration of the carbon source, and (3) the CO_2 concentration of the carbon sink, all of which could be easily obtained in an engineering project, which indicates the convenience of the CP model. However, the CO_2 capture rate which is required in the MGS model is hard to obtain, because it cannot be measured directly.

3.2 Case II: comparative analysis of the CP and TCP models

As described in Sections 2.2 and 2.3, the necessary parameters, which include the reaction temperature and the CO_2 concentration of the carbon source and sink, could be treated as the constraint of both the CP and TCP models. Thus, in this section, the effect of the CO_2 concentration of the carbon source and sink on the w_{ideal} and w_{ideal}' was evaluated, respectively, to compare the CP and TCP models.

As shown in Fig. 6, the w_{ideal} defined in the CP model and the w_{ideal}' defined in the TCP model were calculated using Eqs. (10) and (11), respectively, at a

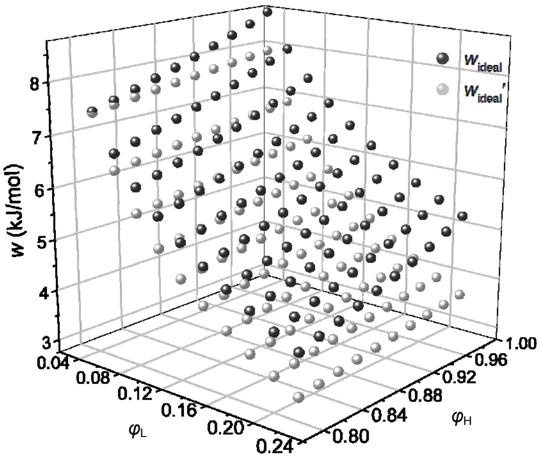

Fig. 6 Comparison between w_{ideal} and w_{ideal}'

Table 2 Comparison of parameters required by the CP and MGS models

Model	Known condition			Constraint condition	
	Reaction temperature	CO_2 concentration	Other	1	2
MGS	45 °C	13.3% (feed gas)	CO_2 capture rate: 90%	Mass conservation of mixed gas	Mass conservation of CO_2
CP	45 °C	13.3% (carbon source)	CO_2 concentration of carbon sink: 98%	Mass conservation of mixed gas	Mass conservation of CO_2

Model	Hypothesis			Formula	Solution quantity
	1	2	3		
MGS	Isothermal and isobaric reversible process	No chemical reaction	Ideal gas mixtures	Wilcox, 2012	Minimum separation work w_{min}
CP	Isothermal and isobaric reversible process	No chemical reaction	Ideal gas mixtures	Eq. (10)	Ideal energy consumption w_{ideal}

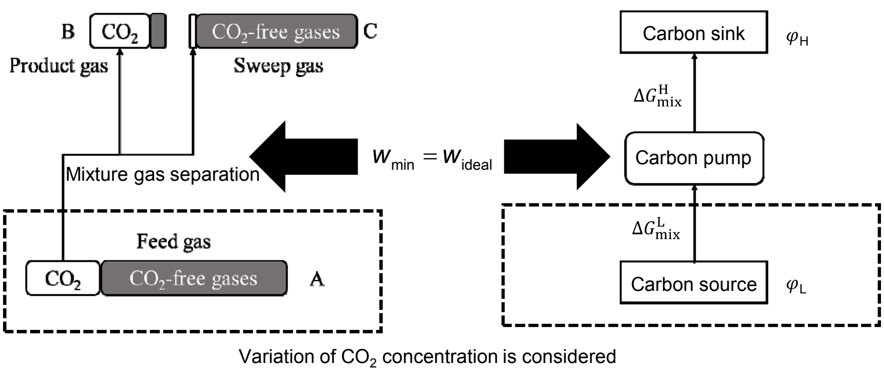

Fig. 5 A schematic diagram of the comparative analysis of the MGS and CP models

reaction temperature of 298 K. The variation trend of these two performance indicators is the same: when the CO_2 concentration of the carbon source is fixed, a higher CO_2 concentration of the carbon sink would lead to a larger work requirement (both w_{ideal} and w_{ideal}'), and when the CO_2 concentration of the carbon sink is fixed, a higher CO_2 concentration of the carbon source would lead to a smaller work requirement (both w_{ideal} and w_{ideal}'). Such a trend was previously proved by Zhao et al. (2017a).

The results also show that w_{ideal}' is always smaller than w_{ideal}, which reflects that the state described in the TCP model more closely approaches the ideal status. We conclude that the most ideal energy consumption of CO_2 capture technology could be determined by applying the TCP model in the thermodynamic aspect (Fig. 7). The advantage of the TCP model derives mainly from the elimination of the irreversibility of gas mixing, as mentioned in Section 2.3.

However, the actual work required in practical CO_2 capture technology would be much greater than w_{ideal}' due to the irreversibility in the actual process, which means that the ideal state described in the TCP model could not be reached in the specific situation. For example, in a flue gas scrubbing technology for CO_2 capture, in which the carbon source cannot be treated with infinite mass capacity because of the requirement to reduce the CO_2 concentration in the feed gas, the w_{ideal}' would be replaced by w_{ideal} and the ideal state could not be reached. However, the technology of DAC is quite different (Section 3.3).

3.3 Case III: application of the TCP model

The concentration of CO_2 in the feed gas (the air, in this case) would also be reduced with the enrichment of CO_2 in DAC. Therefore, in such a technology, the CO_2 concentration of the sweep gas would not need to be controlled because it should be lower than that of the feed gas. Thus, the CO_2 concentration in DAC can be treated as the removal of an infinitesimal amount of CO_2 from the air, and the TCP model could be applied to evaluate the ideal energy consumption, whereas the application of the CP model is not appropriate.

At an ambient temperature of 298 K and pressure of 101.325 kPa, with CO_2 concentration assumed to be 0.04% in the air, and the CO_2 concentration of product gas set to 98%, the w_{ideal}' of DAC measured in the TCP model is 19.334 kJ/mol of CO_2. This is much smaller than the free energy required of the oxidation of carbon to CO_2, which is 395 kJ/mol (Lackner, 2013).

In the process of flue gas scrubbing, assuming that the CO_2 concentration in the flue gas is 20%, the comparison of such a technology with DAC could be clarified with the definition of η as shown in Eq. (16). Such a parameter could be treated as the energy-consumption evaluation of DAC technology, in which the flue gas scrubbing technology is set as standard. Considering that such a "standard" is treated as "energy-intensive" technology in the current stage already, the energy-consumption level of DAC technology could be clarified. In results, η was calculated as 4.916 when these two technologies are in the same reaction condition (here the reaction temperature, ambient pressure, and CO_2 concentration of the product gas are all the same).

$$\eta = \frac{(w'_{ideal})_{DAC}}{(w'_{ideal})_{flue\ gas\ scrubbing}}. \quad (16)$$

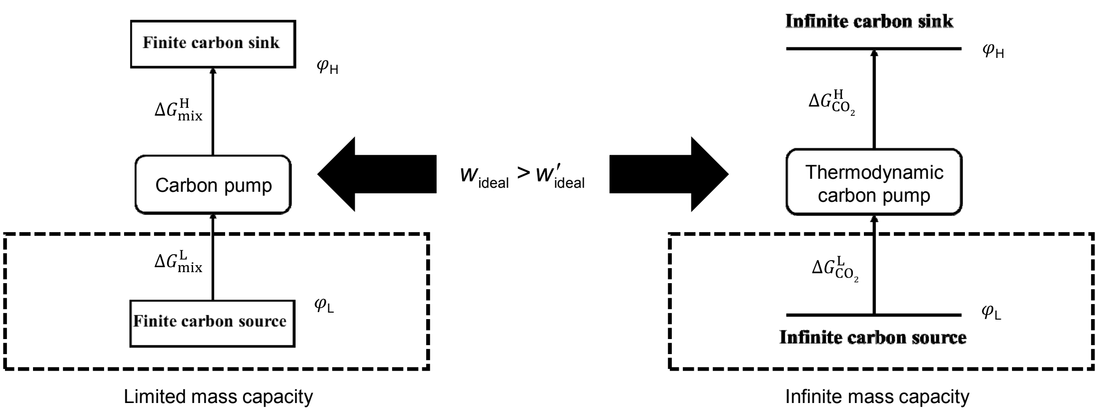

Fig. 7 A schematic diagram of the comparative analysis of the CP and TCP models

The η would drop to 3.68 when the flue gas is 398 K in an actual case, which proves the practical value of the TCP model to evaluate the performance of CO_2 capture technology in the thermodynamic aspect. It is obvious that the minimum ideal energy consumption of flue gas scrubbing increases as the reaction temperature increases, so η decreases at the same time (Fig. 8).

Thus, an interdisciplinary comparison using a classical thermodynamic indicator could be realized, and proves that the energy consumption of DAC is naturally higher than that of flue gas scrubbing technology, indicating that the development of an energy-saving method is still needed for DAC.

3.4 Pros and cons

The relationships among these three thermodynamic theoretical models discussed above are illustrated in Fig. 9. The case listed in Section 3.1 was calculated using each of these three models and the results are shown in Table 3.

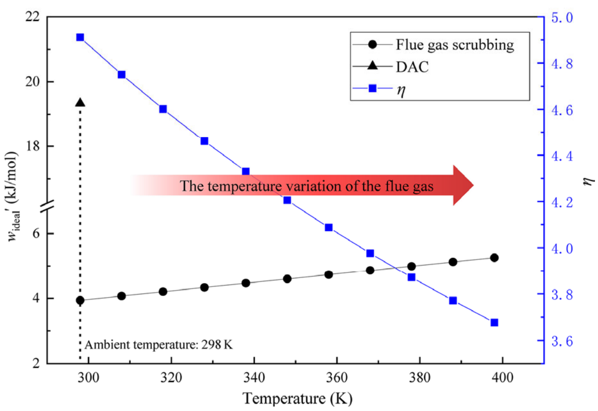

Fig. 8 A comparative analysis of DAC and flue gas scrubbing

Although the MGS model has attracted attention in the current stage of energy-consumption analysis of CO_2 capture, it is not a perfect model. Compared to the MGS model, the CP model is more suitable for evaluation of practical engineering because the known parameters for these two models are different: the concentrations of the CO_2 and gas flow rates from the carbon source and sink are two kinds of parameters required for the CP model to calculate the ideal energy consumption, while the CO_2 capture rate and captured CO_2 capacity are needed for the application of the MGS model. In practice, the carbon source is the exhaust gas and the sink is the product gas, of which the CO_2 concentrations and gas flow rates can be measured directly. Such parameters, which are needed in the CP model, are more conveniently obtained through measurement. In contrast, the capture rate which is needed in the MGS model is more like a setting parameter during the design.

Due to the assumption of mass conservation, the MGS model cannot be expanded to a more ideal physical scenario, but a CP model can be expanded to a TCP model in which carbon sources or sinks have approximately infinite capacity. Such a source and sink could be treated as an analogy of an infinite heat source and sink in the classic Carnot cycle.

With the proposed CP and TCP models, engineering application experience from heat pumps could be directly transferred to these two models, so a

Table 3 Calculation results based on the MGS, CP, and TCP models

w_{min} (kJ/mol)	w_{ideal} (kJ/mol)	w_{ideal}' (kJ/mol)
6.88	6.88	5.28

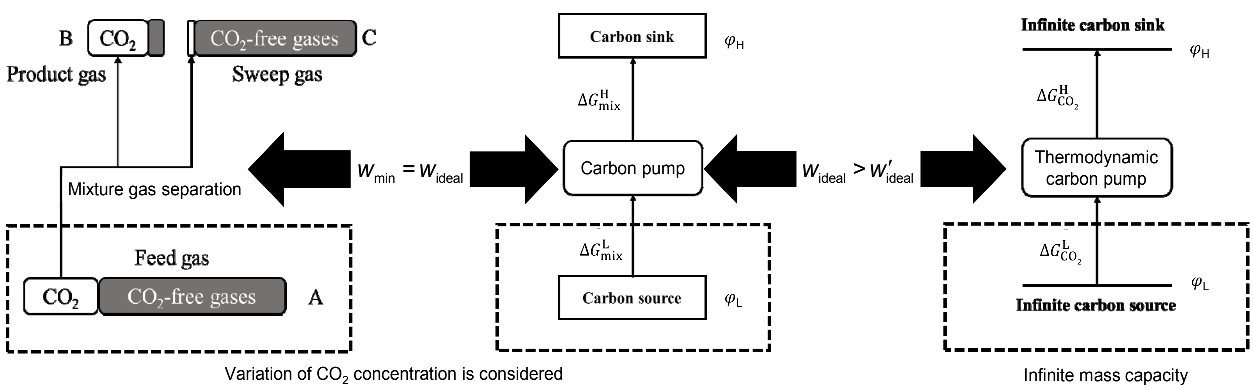

Fig. 9 Relationship between the MGS, CP, and TCP models

thermodynamic carbon pump cycle could be constructed in a CO_2 capture process. With the construction of the thermodynamic cycle, the differences between a real and an ideal cycle could be clarified with an exploration of various irreversibility. These differences, no matter whether caused by entropy production, heat leakage, carbon leakage in the mass transfer process, or power consumed components, would lead to a specific energy-saving guideline to enhance the development of a CO_2 capture system.

4 Conclusions

The integration of a thermodynamic theoretical framework into CO_2 capture was explored in this study, in which the energy conversion mechanism of such a technology was clarified based on the comparative analysis of thermodynamic theoretical models for energy-consumption evaluation. The following conclusions could be drawn following a comparison of three kinds of thermodynamic theoretical models, the MGS, CP, and TCP models:

1. The correctness and convenience of the CP model were indicated by comparison with the MGS model. The ideal energy consumption w_{ideal} calculated by the CP model was proved to be correct, and the convenience of such a model applied in a practical project was also proved.

2. Calculations from the TCP model more closely approached the ideal status than those from the CP model. The ideal minimum energy consumption w_{ideal}' calculated by the TCP model followed the same variation trend as the ideal energy consumption w_{ideal} calculated by the CP model, and the w_{ideal}' proved to be smaller. The irreversibility in the CP model caused by the variation of the CO_2 concentration in the carbon source and sink occurred in an actual situation, such as in flue gas scrubbing technology.

3. The minimum ideal energy consumption of DAC was evaluated with the application of the TCP model and turned out to be 4.916 times that of flue gas scrubbing in the same conditions (except for the CO_2 concentration in the feed gas). The w_{ideal}' of DAC measured in the TCP model was 19.334 kJ/mol of CO_2, when the CO_2 concentration in the air was assumed to be 0.04% (in volume), and the CO_2 concentration of the product gas was set as 98% at an ambient temperature of 298 K and pressure of 101.325 kPa.

Contributors

Shuai DENG designed the research. Yang-zhou ZHOU and Wei-cong XU processed the corresponding data. Shuang-jun LI wrote the first draft of the manuscript. Li ZHAO and Xiang-zhou YUAN helped to organize the manuscript. Ya-wen LIANG revised and edited the final version.

Conflict of interest

Shuang-jun LI, Shuai DENG, Li ZHAO, Wei-cong XU, Xiang-zhou YUAN, Yang-zhou ZHOU, and Ya-wen LIANG declare that they have no conflict of interest.

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中文概要

题　目： 碳捕集能耗分析模型的对比研究

目　的： 碳捕集能耗较高的技术瓶颈，亟待热力学理论在交叉研究中解决。热力学理论工具在碳捕集技术能耗水平评估方面的准确性、有效性和局限性都尚未明确，且碳捕集能耗研究的共性规律仍未被把握。本文对现有能耗分析模型进行对比以揭示碳捕集技术能耗的实质，并提出普适性和针对性恰当的能耗分析模型，以明确碳捕集能耗水平的“天花板”。

创新点： 1. 提出热力学碳泵模型，分析碳捕集技术理想能耗；2. 对比不同碳捕集能耗分析模型，通过案例分析说明其不同特点和理想化程度的差异。

方　法： 1. 通过概念比拟，类比热泵概念，提出热力学碳泵概念，并阐述碳捕集过程是通过热或功驱动的二氧化碳从低浓度向高浓度逆向富集的非自发过程（图 2 和 3），实现碳捕集技术实质的理想化概括；2. 通过热力学理论推导，获得基于热力学碳泵模型的碳捕集最小理想能耗（公式（13））；3. 通过案例分析，论证热力学碳泵模型相对混合气体分离模型和碳泵模型的理想化程度是否更高（图 9），以及其中碳源、汇的无限质容假设是否更接近理想状态。

结　论： 1. 通过碳泵模型可以得到碳捕集技术的理想能耗，并且碳泵模型相对混合气体分离模型在使用时更便捷。2. 热力学碳泵模型相对碳泵模型的理想化程度更高；因为忽略碳源、汇由传质引起的不可逆性，热力学碳泵模型计算所得最小理想能耗比碳泵模型计算所得理想能耗更小。3. 通过热力学碳泵模型分析直接空气碳捕集技术表明，其最小理想能耗是相同反应条件下烟气处理技术的 4.916 倍。

关键词： 碳捕集；能耗；理论模型；热力学碳泵