

# Novel Technique Route of Coal Gasification with CO<sub>2</sub> Capture Using CaO Sorbents via Three-Stage Interconnected Fluidized Beds

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**ABSTRACT:** To modify the temperature mismatch between coal gasification and CO<sub>2</sub> capture in one gasifier, a novel technique route of coal gasification with CO<sub>2</sub> capture via three-stage interconnected fluidized beds (ICFB) was proposed. The three-stage ICFB consisted of a gasifier, an adsorber, and a calcinator, which separated the coal gasification, CO<sub>2</sub> capture, and sorbents regeneration. Also, it could keep the three processes performing at the rational reaction temperatures. A process simulation was constructed on the basis of the chemical and phase equilibrium method using Aspen Plus, and the effects of the adsorption temperature and the steam/coal ratio on adsorption products composition, CO<sub>2</sub> capture efficiency, H<sub>2</sub> yield, and carbon conversion ratio were investigated. The results indicate the adsorption temperature range 600–630 °C and the steam/coal mass ratio range 2.1–2.7 are the possible optimal reaction conditions. The modified process shows an optimal coal gasification with increasing H<sub>2</sub> concentration of 32.60% and capturing CO<sub>2</sub> efficiency of 85.17%, compared with the coal gasification with CO<sub>2</sub> capture in one gasifier.

## 1. INTRODUCTION

Coal gasification is a key enabling technology for a range of efficient and sustainable systems for producing low emissions electricity and other energy products from coal. A good gasification process should provide relatively high H<sub>2</sub> concentration with low (near zero) CO<sub>2</sub> and tar concentrations in the gasification products.<sup>1–3</sup> The gas composition from a fluidized-bed gasifier was investigated by Gil et al.<sup>4</sup> for several gasifying agents (e.g., pure H<sub>2</sub>O, H<sub>2</sub>O–O<sub>2</sub> mixtures, and air). It is clearly showed that relatively high (30–60 vol %, on dry basis) H<sub>2</sub> concentration can be obtained by steam gasification. However, there is always a simultaneous generation of CO<sub>2</sub> and tar, which are undesirable products. There is an increasing interest in new technologies for the hydrogen production and the CO<sub>2</sub> capture in the process of coal gasification,<sup>2</sup> and the objectives can be achieved by an advanced steam gasification with simultaneous CO<sub>2</sub> capture.<sup>5,6</sup>

The cyclic calcination/carbonation reaction (CCCR) of CaO sorbents is considered as an effective approach to capture CO<sub>2</sub> from flue or fuel gas. Compared with the well developed amine adsorption method,<sup>7,8</sup> the CaO sorbent is considered as the predominant absorbing material in the future due to its larger CO<sub>2</sub> absorptive capacity, higher separation efficiency, and lower cost. In 1999, the Japanese Center for Coal Utilization proposed the idea of HyPr-RING (hydrogen production by reaction integrated novel gasification) based on dual fluidized beds.<sup>9–11</sup> In 2009, Abanades et al. built up dual fast fluidized beds reactors based on the CCCR technique, which marked the CCCR research had turned from the sorbents property to industrial applications.<sup>12</sup> Ramkumar et al. researched the CCCR technique and analyzed the promoting effects of CaO sorbents on producing H<sub>2</sub> and capturing CO<sub>2</sub>. CaO sorbents had been found to enhance H<sub>2</sub> yield to a large extent, even in the absence of water–gas shift catalysts.<sup>6</sup> Generally, to improve the sorbents performance<sup>13</sup> and to study the fluidized bed system based on CCCR are the key focuses.<sup>6,12,14</sup>

Based on the 1 kW two-stage interconnected fluidized beds (ICFB) built at Southeast University, Zhao et al. carried out a study on coal gasification with in situ CO<sub>2</sub> capture using CaO sorbents.<sup>15</sup> The two-stage ICFB includes two reactors: a gasifier and a calcinator. In the gasifier, coal is gasified with steam, and simultaneously, CaO sorbents react with CO<sub>2</sub> to produce CaCO<sub>3</sub> (i.e., CaO sorbents carbonation). The coal gasification and CO<sub>2</sub> removal are integrated in the gasifier. In the calcinator, unreacted chars from the gasifier are combusted with air, and meanwhile, the calcination reaction takes place. CaCO<sub>3</sub> is decomposed to CO<sub>2</sub> and CaO (i.e., CaO sorbents regeneration).<sup>16,17</sup> The technique route potentially eliminates the requirement for the catalysts of water–gas shift reaction.<sup>6,18</sup>

Although it is observed that H<sub>2</sub> concentration in gasification products was increased and CO<sub>2</sub> was captured, the results were not quite satisfied.<sup>15</sup> CO<sub>2</sub> cannot be absorbed by CaO sorbents when the gasification temperature exceeds 720 °C in the two-stage ICFB, while the CO<sub>2</sub> capture efficiency is only about 9.00% at 700 °C with a low carbon conversion ratio.<sup>15</sup> Further experimental and simulation studies by Zhao et al. demonstrated that there was a distinct defect in the coal gasification with in situ CO<sub>2</sub> capture via two-stage ICFB.<sup>15,19</sup> At atmospheric pressure, the rational temperature for CaO sorbents capturing CO<sub>2</sub> ranges from 615 to 655 °C,<sup>20</sup> while that for coal gasification should exceed 900 °C at current state-of-art.<sup>21</sup>

To improve H<sub>2</sub> concentration and CO<sub>2</sub> capture efficiency, this paper presents a novel coal gasification process with CO<sub>2</sub> capture via three-stage ICFB system. It mainly consists of a gasifier, an adsorber, and a calcinator, where coal gasification, CO<sub>2</sub> capture, and sorbents regeneration can take place at correspondingly optimal temperatures, respectively. This study

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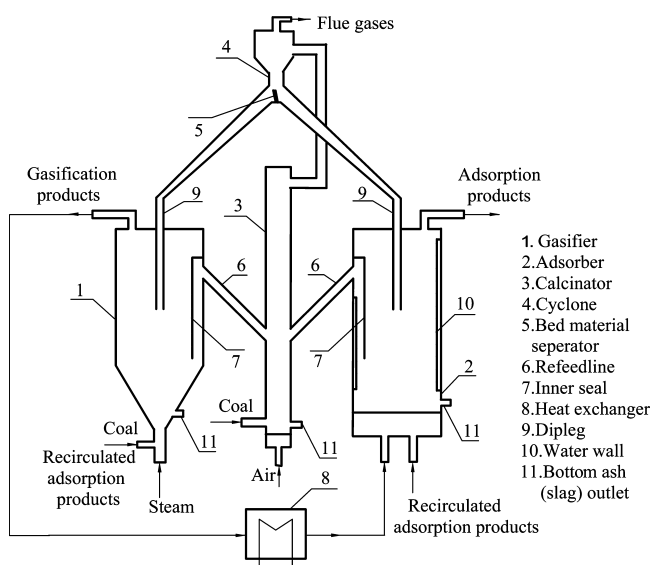
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first proposed and described the novel technique route via the three-stage ICFB. Subsequently, a simulation using Aspen Plus was carried out to investigate the feasibility and efficiency of the process. It focused on the effects of the adsorption temperature and the steam/coal ratio on adsorption products composition, CO<sub>2</sub> capture efficiency, carbon conversion ratio, and H<sub>2</sub> yield.

## 2. PROCESS DESIGN AND SIMULATION

**2.1. Process Configuration.** The scheme of the three-stage ICFB is shown in Figure 1. It consists of a gasifier, an



**Figure 1.** Scheme of coal gasification with CO<sub>2</sub> capture in the three-stage ICFB.

adsorber, calcinator, a cyclone, a bed materials separator, two refeedlines, two inner seals, two downcomers, a heat exchanger, and a water wall. Preliminarily, based on our existing two-stage ICFB,<sup>15–17</sup> we recommended a spout-fluid bed, a bubbling fluidized bed, and a fast fluidized bed for the gasifier, adsorber, and calcinator, respectively. The fluidization regime for the calcinator is recommended as fast fluidization, while the fluidization regimes for the gasifier and adsorber are bubbling fluidizations. However, the design and configuration may not be limited to the recommendation. The middle of the calcinator is connected with the gasifier and the adsorber by refeedlines, and the top is connected with a cyclone. The two downcomers of the cyclone are inserted into the tops of the gasifier and the adsorber, respectively, and the bed materials separator is located in the bottom of the cyclone. Besides, the water wall is arranged on the internal surface of the adsorber. The mixtures of sands, CaO sorbents, and catalysts (Ni or Fe based) are used as bed materials.

In the gasifier, the reaction temperature is around 900–950 °C. The heat needed for coal gasification is transferred from the calcinator by bed materials. As soon as coal particles are fed into the reactor by relatively low-speed steam from the bottom, an exquisite heat contact takes place among coal particles, steam, and bed materials, and a bubbling fluidization regime forms. Coal particles are rapidly heated to the bed temperature and gasified with steam. Bed materials and unreacted chars get back to the calcinator by the refeedline, while gasification products escape from top of the gasifier, mainly consisting of H<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and steam.

High-temperature gasification products are cooled down by the heat exchanger and then enter the bottom of the adsorber with a relative low velocity. CaO sorbents enter the top of the adsorber by the downcomer and react with CO<sub>2</sub> in the gasification products to produce CaCO<sub>3</sub>, that is, sorbents carbonation, which is an exothermic reaction. The adsorber can be kept at a bubbling fluidization regime; meanwhile, it can be easily overheated by the high-temperature bed materials from calcinator and the released heat from the exothermic carbonation reaction. The water wall arranged on the internal surface is designed to keep the adsorber at around 600–700 °C. The adsorption products, mainly containing H<sub>2</sub>, CH<sub>4</sub>, CO, and steam, are exhausted from the top of the adsorber, while CaCO<sub>3</sub> and bed materials get back to the calcinator by the refeedline.

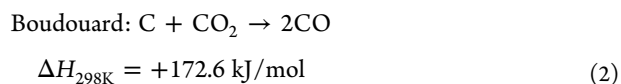
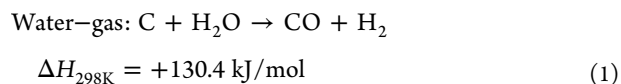
In the calcinator, coal particles are delivered into the reactor from the bottom, and air serves as the fluidized wind and the oxidizing agent. The calcinator is kept at a fast fluidization regime because of the high-speed air flow. The reaction temperature is operated at around 950–1000 °C. CaCO<sub>3</sub> from the two refeedlines decomposes into CaO and CO<sub>2</sub>. The bed materials are separated from flue gas (which mainly consists of CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>) through a cyclone and then get back to the gasifier and the adsorber, while flue gas is exhausted from the top of the cyclone.

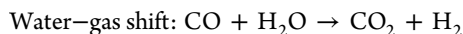
Bottom ash (slag) is collected from the bottom ash outlet of the reactors. Fly ash is a fine powder, which has smaller particle size than that of bed materials. Fly ash can be separated from the top of the spout-fluid bed and by the cyclone.<sup>22</sup> Additionally, due to attrition, a tiny fraction of bed materials can break into smaller particles. The part of bed material particles may be entrained out along with fly ash was ignored in this study. It will not contribute much to the performance of the whole process.

There is an inner seal in the gasifier and the adsorber, respectively.<sup>23</sup> The inner seal allows particles (including reactants) to move from the gasifier or the adsorber to the calcinator, but prevents the bypassing of the gas from the opposite direction. Moreover, there is a bed materials separator in the bottom of the cyclone. As needed, it can be designed to distribute the bed materials entering the gasifier and the adsorber from the cyclone. The detailed design of the bed materials separator is not studied in this paper. From the perspective of industry, part of adsorption products can be recirculated as the fluidized wind, which is fed into the bottom of the gasifier and the adsorber to further increase H<sub>2</sub> concentration.

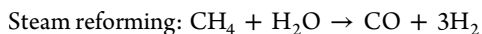
Compared with coal gasification with in situ CO<sub>2</sub> capture in the two-stage ICFB, the novel coal gasification process presented here makes sure that coal gasification, CO<sub>2</sub> capture by CaO sorbents, and sorbents regeneration can perform at the optimal reaction temperatures, which is a potential way to increase the H<sub>2</sub> concentration and CO<sub>2</sub> capture efficiency.

**2.2. Thermodynamic Analysis of the Reactions.** The main reactions involved in the system are as follows:

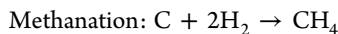




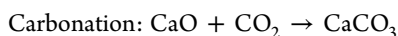
$$\Delta H_{298\text{K}} = -42.2 \text{ kJ/mol} \quad (3)$$



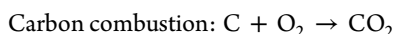
$$\Delta H_{298\text{K}} = +205.3 \text{ kJ/mol} \quad (4)$$



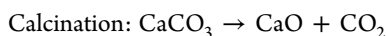
$$\Delta H_{298\text{K}} = -74.9 \text{ kJ/mol} \quad (5)$$



$$\Delta H_{298\text{K}} = -178.2 \text{ kJ/mol} \quad (6)$$



$$\Delta H_{298\text{K}} = -393.5 \text{ kJ/mol} \quad (7)$$



$$\Delta H_{298\text{K}} = +178.2 \text{ kJ/mol} \quad (8)$$

where, R 1–R 5 perform in the gasifier; R 3, R 4, and R 6 perform in the adsorber; and R 7 and R 8 mainly perform in the calcinator. According to standard Gibbs free energy function, the relations between the equilibrium coefficient  $K_p$  and the reaction temperature  $T$  for the main reactions are shown in Figure 2.

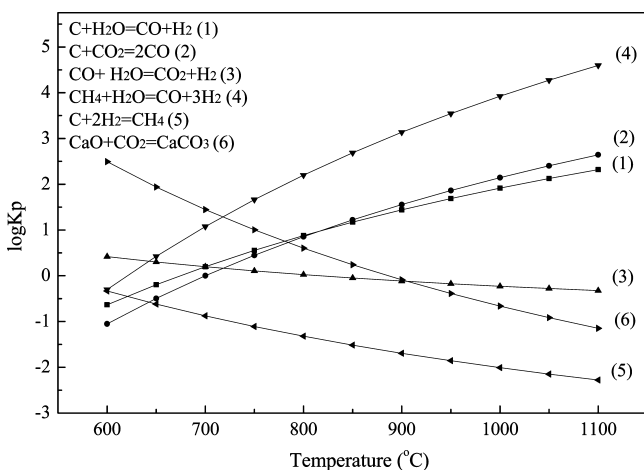


Figure 2. Relations between  $K_p$  of the main reactions and  $T$ .

The gasification products and adsorption products are due to a series of reactions including R 1–R 6. Water–gas R 1, Boudouard R 2, and steam reforming R 4 are intensive endothermic reactions, while water–gas shift R 3, methanation R 5, and carbonation R 6 are exothermic reactions. High temperature is more favorable to the reactants in exothermic reactions and the products in endothermic reactions. R 1 is the determining step in the gasifier,<sup>24,25</sup> and appropriate higher temperature will accelerate the process. Similarly, high temperature will promote  $\text{CaCO}_3$  to decompose in the calcinator. The equilibrium coefficient of R 6 drops with the temperature rising in the adsorber, which means relatively lower temperature will be in favor of absorbing  $\text{CO}_2$  by  $\text{CaO}$ ; however, excessive low temperature can, in turn, decelerate R 6

and decrease the  $\text{CO}_2$  capture efficiency. For this reason, proper adsorption temperature should be determined.

**2.3. Process Parameters.** To evaluate the process performance of the three-stage ICFB, three parameters were applied and defined as follows:

**$H_2$  Yield.**  $H_2$  yield is used to evaluate the status of producing  $H_2$  in the whole system; it is defined as

$$H_2 \text{ yield} = \frac{F_{H_2,a}}{F_{C,gc}} \quad (9)$$

where,  $F_{H_2,a}$  is the mass flow of  $H_2$  at the outlet of the adsorber, in g/h, and  $F_{C,gc}$  is the mass flow of coal fed into the gasifier and the calcinator, in kg/h.

**$\text{CO}_2$  Capture Efficiency.**  $\text{CO}_2$  capture efficiency is used to evaluate the  $\text{CO}_2$  capture performance of  $\text{CaO}$  sorbents; it is defined as

$$\text{CO}_2 \text{ capture efficiency} = \frac{F_{\text{CO}_2,g} - F_{\text{CO}_2,a}}{F_{\text{CO}_2,g}} \times 100 \quad (10)$$

where  $F_{\text{CO}_2,g}$  and  $F_{\text{CO}_2,a}$  are the mass flows of  $\text{CO}_2$  at the outlet of the gasifier and the adsorber, respectively, in kg/h.

**Carbon Conversion Ratio.** The carbon conversion ratio is used to evaluate the degree of coal effective utilization to produce hydrogen-rich gas; it is defined as

$$\text{carbon conversion ratio} = \frac{F_{C,g}}{F_{C,gc}} \times 100 \quad (11)$$

where  $F_{C,g}$  is the mass flow of coal fed into the gasifier, in kg/h.

Three operational parameters are as follows:

**Steam/Coal Ratio.** It is defined as

$$\text{steam/coal ratio} = \frac{F_{\text{ste},g}}{F_{C,g}} \quad (12)$$

where  $F_{\text{ste},g}$  is the mass flow of steam fed into the gasifier, in kg/h.

**Air/Coal Ratio.** It is defined as

$$\text{air/coal ratio} = \frac{F_{\text{air},c}}{F_{C,c}} \quad (13)$$

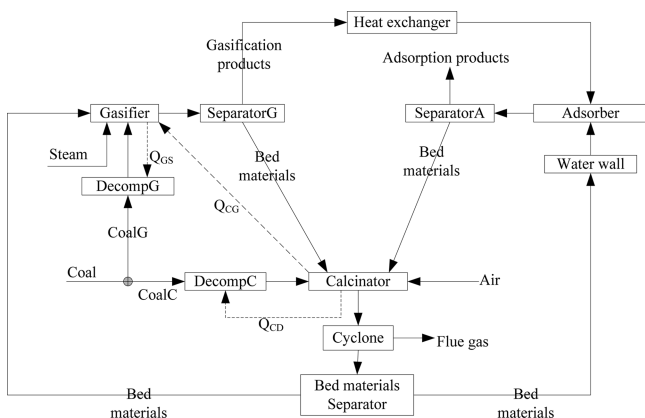
where  $F_{\text{air},c}$  and  $F_{C,c}$  are the mass flows of air and coal fed into calcinator, respectively, in kg/h.

**Bed Materials Distribution Ratio.** The bed materials distribution ratio is used to determine the amount of bed materials distributed to the gasifier and adsorber, respectively, from the cyclone. It is regulated by the bed materials separator in the bottom of the cyclone, and it is defined as

$$\text{bed materials distribution ratio} = \frac{F_{\text{bm},a}}{F_{\text{bm},cyc}} \quad (14)$$

where,  $F_{\text{bm},a}$  is the mass flow of bed materials enters the adsorber from the cyclone outlet, in kg/h;  $F_{\text{bm},cyc}$  is the mass flow of bed materials at the inlet of the cyclone, in kg/h.

**2.4. Process Simulation.** **2.4. Blocks and Streams Description.** According to the process design described in section 2.1, the simulation is presented graphically in Figure 3. Generally, there are two categories of methods for simulation on such a process: (a) chemical and phase equilibrium method and (b) kinetic method. The chemical and phase equilibrium method was chosen mainly for two reasons: First, considering



**Figure 3.** Simulation of coal gasification with CO<sub>2</sub> capture in three-stage ICFB.

the excellent catalytic activity of some catalysts, it could be approximately considered that the catalysts will result in a chemical and phase equilibrium at a specified temperature. Second, it is applicable to study the feasibility and the optimal process performance of the novel coal gasification process, which this study focused on. It does not deserve further investigations if the process is infeasible or its optimal performance has no significant advantage. The equilibrium reactors were chosen without considering of the difference of the bed types. Either gasifier or calcinator was simulated by a combination of a Ryield model and a RGibbs model. As coal was treated as a nonconventional component by Aspen Plus, a Ryield model was used to decompose coal into conventional components based on the mass balance, of which the behaviors can be further simulated by the RGibbs model. The adsorber and water wall were simulated by a RGibbs model and a Heater model, respectively. All the RGibbs models were restricted by the chemical and phase equilibriums. The cyclone and the bed materials separator were simulated by separator models. For practical operation, the adsorption product gas can be recycled to serve as fluidization wind of the gasifier and the adsorber; however, it is not modeled in the simulation to simplify calculation of H<sub>2</sub> yield and CO<sub>2</sub> capture efficiency.<sup>17</sup>

Based on the principles of Aspen Plus, the simulation was modeled based on following assumptions:<sup>17,26</sup>

- (1) The coal gasification products mainly contain CO, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, N<sub>2</sub>, H<sub>2</sub>S, COS, and SO<sub>2</sub>; tar was not taken into account in this simulation.
- (2) Ash is treated as inert component and does not react with gasification products or sorbents.
- (3) The reactors were operated under a steady state, and the residence time was long enough for the reactions to achieve chemical and phase equilibriums.
- (4) The pressure losses in the reactors and pipes were ignored in this simulation.

**Energy Balance.** The heat duties of the heat exchanger and the water wall can be easily removed, for example, by varying the mass flow of the cooling medium (water). It means that,

from the perspective of energy, the cooling of the gasification products and bed materials prior to the adsorber is relatively independent; only the energy balance between the gasifier and calcinator is coupled in the case of this study. The mass flow of coal stream fed into the system is constant, and then, the coal stream is split into two substreams for gasification and calcinations, respectively. In order to keep the energy balance between the gasifier and calcinator, a design specification provided by Aspen Plus was modified to assign the proportions of the substreams automatically.

**Operational Parameters.** The operational condition and main parameters in this simulation are as follows:

- (1) The three-stage ICFB system is operated at atmospheric pressure.
- (2) The total mass flow of coal fed to the system is 100 kg/h at 25 °C.
- (3) The circulation of the CaO sorbents in bed materials is 180 kg/h, and the bed materials distribution ratio is assumed to be 0.7 in this study.
- (4) The temperature of inlet air is 25 °C and the air/coal ratio is 9.7.
- (5) The temperature of steam fed into the gasifier is 450 °C, and the steam/coal ratio ranges from 0.9 to 3.6.
- (6) The temperatures of the adsorption products and bed materials at the outlet of the heat exchanger and water wall, respectively, are controlled to be the same as that of the adsorber.
- (7) The gasifier and calcinator are operated at 925 and 975 °C, respectively, and the adsorption temperature with range from 600 to 700 °C is investigated.

In this study, Shenhua bitumite is used as feedstock, of which the proximate and ultimate analyses, on a measured basis, are as listed in Table 1.

### 3. RESULT AND DISCUSSION

**3.1. Effects of Adsorption Temperature.** The adsorption temperature significantly influences the chemical equilibrium in adsorber, and further influences the composition of adsorption products. The effects of the adsorption temperature range 600–700 °C were investigated with a constant steam/coal ratio of 2.7. The temperatures of gasifier and calcinator were kept constant.

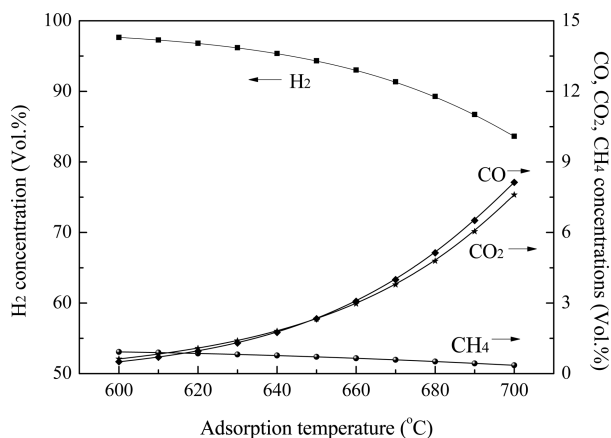
**Effects on Adsorption Products Composition.** As the adsorption temperature rises from 600 to 700 °C (Figure 4), H<sub>2</sub> concentration drops from 97.65% to 83.63% (on dry basis), while CO and CO<sub>2</sub> concentration increase from 0.50% to 8.13% and from 0.63% to 7.60%, respectively. Additionally, the CH<sub>4</sub> concentration decreases slightly.

The reasons might be as follows, the increase of adsorption temperature will distinctly undermine the carbonation R 6, causing CO<sub>2</sub> concentration to increase highly in the adsorber. In another word, high temperature decreases the capture performance of CaO sorbents, as a result of which, less CO<sub>2</sub> is absorbed. With the rising of CO<sub>2</sub> concentration, water–gas R 3 is promoted to shift toward the backward direction, and thus, CO concentration increased, while H<sub>2</sub> concentration decreased.

**Table 1.** Proximate Analysis and Ultimate Analysis of Coal

|    | proximate analysis (wt %, air-dried basis) |           |              |      | ultimate analysis (wt %, air-dried basis) |      |       |      |      |             |
|----|--|-----------|--------------|------|---|------|-------|------|------|-------------|
|    | moisture                                   | volatiles | fixed carbon | ash  | C   | H    | O     | N    | S    | LHV (MJ/kg) |
| SH | 6.01                                       | 35.10     | 54.13        | 4.76 | 69.57                                     | 4.30 | 13.81 | 1.03 | 0.52 | 27.1        |

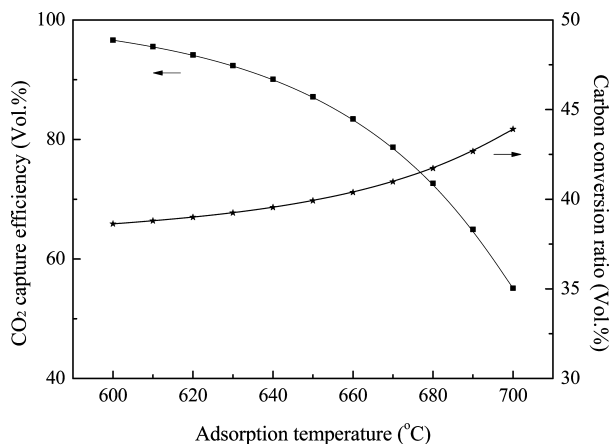




**Figure 4.** Effects of adsorption temperature on adsorption products composition (on dry basis).

Meanwhile, the increase of adsorption temperature directly promotes the water–gas R 3 to shift to the reactants. Because of the limit of chemical equilibrium coefficient, a high steam/coal ratio of 2.7 will lead to a low  $\text{CH}_4$  equilibrium concentration in steam reforming R 4. In sum, 600–640 °C is a favorable temperature range to obtain a higher  $\text{H}_2$  concentration, as well as lower concentrations of CO and  $\text{CO}_2$ .

**Effects on  $\text{CO}_2$  Capture Efficiency and Carbon Conversion Ratio.** As shown in Figure 5, with the adsorber temperature

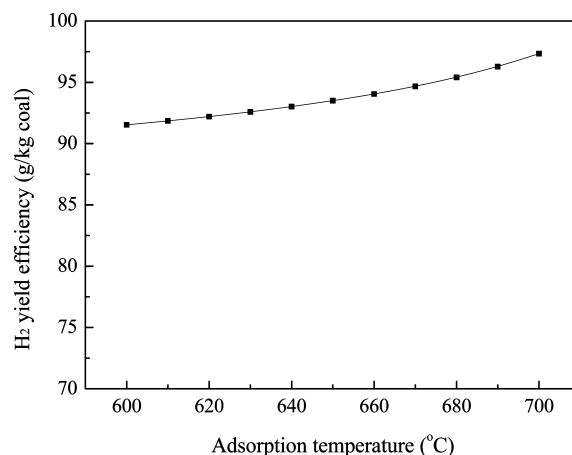


**Figure 5.** Effects of adsorption temperature on  $\text{CO}_2$  capture efficiency and carbon conversion ratio.

increasing,  $\text{CO}_2$  capture efficiency drops sharply from 96.62% at 600 °C to 55.11% at 700 °C, while the carbon conversion ratio slightly increases from 38.63% to 43.91%.

The result of  $\text{CO}_2$  capture efficiency in Figure 5 corresponds with the variance trend of  $\text{CO}_2$  concentration in Figure 4, which clearly indicates that the  $\text{CO}_2$  capture performance of CaO sorbents declines with adsorption temperature rising. Additionally, because the temperatures of calcinator and gasifier are kept nearly constant, the temperature difference between calcinator and adsorber decreases. Then, less coal needs to be burned in the calcinator to heat up bed materials. In other words, more coal is fed into the gasifier, leading to a slight increase in carbon conversion ratio.

**Effects on  $\text{H}_2$  Yield.** Figure 6 shows that  $\text{H}_2$  yield increases gradually from 91.53 g/kg coal to 97.34 g/kg coal with the



**Figure 6.** Effects of adsorption temperature on  $\text{H}_2$  yield.

adsorber temperature increasing from 600 to 700 °C, which is opposite to the variance of  $\text{H}_2$  concentration in Figure 4.

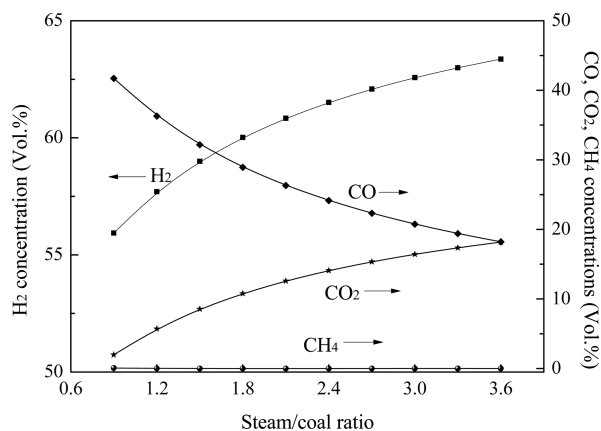
The discrepancy might be explained by the following reason. As indicated in Figure 5, the carbon conversion ratio increases with an increase in adsorption temperature, which means more coal are gasified and more gasification products are produced. Therefore, it leads to an increase in mass flow of  $\text{H}_2$ , that is, an increase in  $\text{H}_2$  yield. Generally,  $\text{H}_2$  concentration is suitable for evaluating the quality of fuel gas, while the  $\text{H}_2$  yield is a preferred parameter to assess the economic performance of the system.

As a whole, according to the analyses of Figures 4–6, the effects of adsorption temperature on the carbon conversion ratio and  $\text{H}_2$  yield might not be significant, compared with that on  $\text{H}_2$  concentration and  $\text{CO}_2$  capture efficiency. Therefore, a relatively lower adsorption temperature range of 600–630 °C is recommended to obtain the adsorption products with higher  $\text{H}_2$  concentration and lower CO and  $\text{CO}_2$  concentrations.

**3.2. Effects of Steam/Coal Ratio.** The steam/coal ratio is another vital factor that influences product gas composition (especially for  $\text{H}_2$  and  $\text{CH}_4$  concentrations). The effects of the steam/coal ratio were investigated based on simulation results with a possibly optimal adsorption temperature of 620 °C. The temperatures of gasifier and calcinator were also kept constant. The steam/coal ratio varies from 0.9 to 3.6, and its effects are presented as follows.

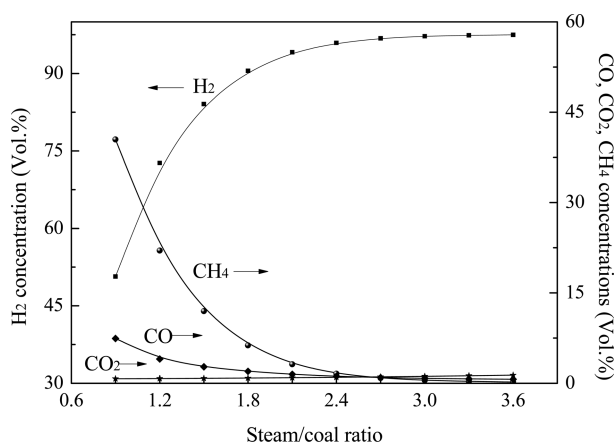
**Effects on Gasification Products and Adsorption Compositions.** As for the effects on the gasification products, Figure 7 shows that, with the increase in steam/coal ratio,  $\text{H}_2$  and  $\text{CO}_2$  concentrations increase distinctly, while CO concentration presents an opposite variance trend. In addition,  $\text{CH}_4$  concentration is extremely low. The reasons might be as follows: Because of the increase of steam/coal ratio, steam of higher concentration promotes water gas R 1, water–gas shift R 3, and steam reforming R 4 to shift toward the forward direction, causing an increase in  $\text{H}_2$  and  $\text{CO}_2$  concentrations. Additionally, though R 1 tends to increase CO concentration as the steam/coal ratio rises, it is the reason that R 3 becomes more dominant, of which the equilibrium shifts to the direction of reducing CO concentration. At the high temperature of 925 °C,  $\text{CH}_4$  concentration stays small because of the limit of the equilibrium coefficient of R 4.

After the gasification products are cooled and fed into the adsorber,  $\text{CO}_2$  in the gasification products is captured by CaO sorbents. The composition of adsorption products is as shown



**Figure 7.** Effects of steam/coal ratio on gasification products composition (on dry basis).

in Figure 8. As the steam/coal ratio increases from 0.9 to 3.6, H<sub>2</sub> and CO<sub>2</sub> concentrations increase from 50.67% to 97.48%



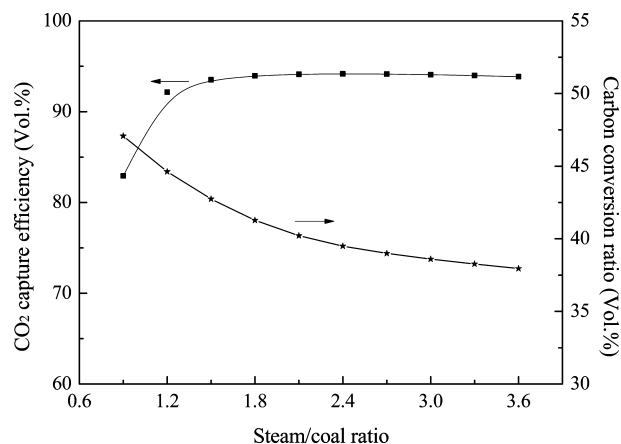
**Figure 8.** Effects of steam/coal ratio on adsorption products composition (on dry basis).

and from 0.76% to 1.35%, respectively, on dry basis, while CO concentration drops. In addition, CH<sub>4</sub> concentration drops sharply from 40.48% to 3.16%, on dry basis, with the steam/coal ratio rising from 0.9 to 2.1, and then stays very low. The reasons might be as follows: With the increase in the steam/coal ratio, R 3 and R 4 are promoted to produce more H<sub>2</sub>, and the reason for the decrease of CO is similar to that in the analysis of Figure 7. The variance of CH<sub>4</sub> in Figures 7 and 8 might be the result of different temperatures and steam contents in the gasifier and calcinator. The adsorption temperature and steam content in the adsorber is lower than that in the gasifier. Thus, according to the thermodynamic analysis in section 2.2, the CH<sub>4</sub> equilibrium concentration of R 4 in the adsorber is considerably higher than that in the gasifier (as the results show, for example, at the steam/coal ratio of 0.9, CH<sub>4</sub> concentration is 40.48% in the adsorber, compared to 0.08% in the gasifier).

Based on the analyses in Figures 7 and 8, it can be concluded that a relatively high steam/coal ratio will promote the H<sub>2</sub> production, as well as decrease CO and CO<sub>2</sub> concentrations in adsorption products in general. More importantly, a higher steam/coal ratio will substantially decrease CH<sub>4</sub> concentration in adsorption products within the investigated temperatures.

Therefore, the adsorption products are more favorable when the steam/coal ratio is higher than 2.1. Besides, the results in Figures 7 and 8 imply a potential technique route to produce methane-rich gas by regulating water/coal ratio via the three-stage ICFB.

**Effects on CO<sub>2</sub> Capture Efficiency and Carbon Conversion Ratio.** As shown in Figure 9, the CO<sub>2</sub> capture efficiency



**Figure 9.** Effects of steam/coal ratio on CO<sub>2</sub> capture efficiency and carbon conversion ratio.

increases from 82.93% to 93.52% when the steam/coal ratio increases from 0.9 to 1.5. It reaches the maximum value of 94.17% at the steam/coal ratio of 2.4 and then stays nearly constant. On the contrary, the carbon conversion ratio decreases gradually from 47.08% to 37.95% with the steam/coal ratio varying from 0.9 to 3.6.

When the steam/coal ratio is small, Figure 7 indicates that CO<sub>2</sub> concentration in the gasification products is very low, and CaO sorbents capture a small amount of CO<sub>2</sub> in the adsorber because of the rarefied CO<sub>2</sub> in the gas, resulting in a low CO<sub>2</sub> capture efficiency. On the other hand, when the steam/coal ratio exceeds 1.8, the effects of the steam/coal ratio on CO<sub>2</sub> concentration (Figures 7 and 8) and CO<sub>2</sub> capture efficiency (Figure 9) become weakened. In terms of the carbon conversion ratio, the larger the steam/coal ratio is, the more steam is fed into the gasifier. Subsequently, more coal needs to be combusted in the calcinator to heat steam to the gasification temperature. Then, it causes a decrease in the carbon conversion ratio of the system. In other words, excessive steam/coal ratio will decrease the economic performance via the three-stage ICFB.

**Effects on H<sub>2</sub> Yield.** With the steam/coal ratio increasing from 0.9 to 2.7, the H<sub>2</sub> yield substantially increases from 26.29 g/kg coal to 92.20 g/kg coal (Figure 10). H<sub>2</sub> yield reaches maximum of 92.72 g/kg coal at the steam/coal ratio of 3, and then, it stays nearly constant. The variance trend of H<sub>2</sub> yield is in line with the result presented by other literature.<sup>17</sup>

The result might be explained by the following reason: For the steam/coal ratio lower than 2.7, there is not enough steam to participate in R 3 and R 4, which means the increase of the steam/coal ratio will promote R 3 and R 4 and improve the H<sub>2</sub> yield considerably. However, when the steam/coal ratio is higher than 3, the effect on H<sub>2</sub> yield becomes weakened.

By summarizing the results of Figures 7–10, it can be concluded that H<sub>2</sub> concentration and yield will be promoted considerably with the steam/coal ratio increasing, and CH<sub>4</sub>,

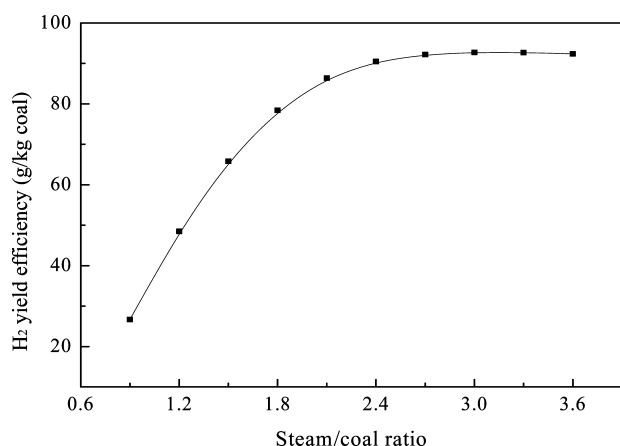


Figure 10. Effects of steam/coal ratio on H<sub>2</sub> yield.

CO, and CO<sub>2</sub> concentrations will be effectively reduced simultaneously. Additionally, the carbon conversion ratio will decrease. Thus, the steam/coal ratio range 2.1–2.7 is favorable at the adsorption temperature of 620 °C, which results in a qualified hydrogen-rich product gas as well as a good carbon conversion ratio.

In summary, according to the results in the previous technique route via two-stage ICFB, the maximal H<sub>2</sub> concentration (on dry basis) and CO<sub>2</sub> capture efficiency are 63.34% and 9.00%, respectively.<sup>15</sup> However, the modified process in this paper indicates that the H<sub>2</sub> concentration (on dry basis) and CO<sub>2</sub> capture efficiency can be up to 95.94% and 94.17%, respectively, according to the equilibrium model. Thus, based on chemical and phase equilibrium methods, the modified process shows an approximate optimal coal gasification with increasing H<sub>2</sub> concentration of 32.60% and capturing CO<sub>2</sub> efficiency of 85.17%, compared with the previous technique routes. The key process performances at the possible optimal adsorption temperature of 620 °C and steam/coal ratio of 2.4 are shown in Table 2.

Table 2. Key Process Performances at Adsorption Temperature of 620 °C and Steam/Coal Ratio of 2.4

| performance                                | value           |
|--|-----------------|
| Composition of Adsorption Products (vol %) |                 |
| CO   | 1.16            |
| CO <sub>2</sub>                            | 0.99            |
| CH <sub>4</sub>                            | 1.6             |
| H <sub>2</sub>                             | 95.94           |
| N <sub>2</sub>                             | 0.31            |
| CO <sub>2</sub> capture efficiency         | 94.17           |
| carbon conversion ratio                    | 39.50           |
| H <sub>2</sub> yield                       | 90.48 g/kg coal |

#### 4. CONCLUSION

A novel technique route of coal gasification with CO<sub>2</sub> capture via three-stage ICFB was proposed to modify the temperature mismatch of coal gasification and CO<sub>2</sub> capture in the gasifier. The three-stage ICFB separates coal gasification, CO<sub>2</sub> capture by CaO sorbents, and sorbents regeneration, and it could keep the three processes performing at the individual optimal temperature ranges.

Based on chemical and phase equilibrium methods, the simulation results indicate that the adsorption temperature range of 600–630 °C and steam/coal ratio range 2.1–2.7 are recommended for the process via three-stage ICFB. At an adsorption temperature of 620 °C and a steam/coal ratio of 2.4, H<sub>2</sub> concentration, H<sub>2</sub> yield, CO<sub>2</sub> capture efficiency, and carbon conversion ratio are 95.94%, 90.48 g/kg coal, 94.17%, and 39.50%, respectively.

The novel process via three-stage ICFB shows excellent process performances compared with that of previous technique routes. Though there is a long distance from commercial use, the excellent process performances show that this novel coal gasification process and related equipment design merits further studies, such as entire process modeling, economic assessment, chemical kinetics, and hydrodynamics, etc.

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##### Notes

The authors declare no competing financial interest.

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#### NOMENCLATURE

$K_p$  = equilibrium coefficient

$T$  = the reaction temperature, in K or °C

$F_{H_2,a}$  = the mass flow of H<sub>2</sub> at the outlet of the adsorber, in g/h

$F_{C,gc}$  = the mass flow of coal fed into the gasifier and the calcinator, in kg/h

$F_{CO_2,g}$  = the mass flows of CO<sub>2</sub> at the outlet of the gasifier, in kg/h

$F_{CO_2,a}$  = the mass flows of CO<sub>2</sub> at the outlet of the adsorber, in kg/h

$F_{C,g}$  = the mass flow of coal fed into the gasifier, in kg/h

$F_{ste,g}$  = the mass flow of steam fed into the gasifier, in kg/h

$F_{air,c}$  = the mass flows of air fed into the calcinator, in kg/h

$F_{C,c}$  = the mass flows of coal fed into the calcinator, in kg/h

$F_{bm,a}$  = the mass flow of bed materials enters the adsorber from the cyclone outlet, in kg/h

$F_{bm,cyc}$  = the mass flow of bed materials at the inlet of the cyclone, in kg/h

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