Reduction of Iron Oxide as an Oxygen Carrier by Coal Pyrolysis and Steam Char Gasification Intermediate Products

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Reduction of Iron Oxide as an Oxygen Carrier by Coal Pyrolysis and Steam Char Gasification Intermediate Products

Jing-biao Yang, Ning-sheng Cai,* and Zhen-shan Li

Key Laboratory of Thermal Science and Power Engineering of Ministry of Education, Department of Thermal Engineering, Tsinghua University, Beijing 100084, China

The feasibility of the reduction of oxygen carrier Fe_2O_3 in chemical-looping combustion using solid fuel (lignite) provided a gasifying agent like steam was introduced into the reactor was investigated with a fixed-bed reactor. The X-ray diffractometer and scanning electron microscope were used for the characterization of the Fe_2O_3 and its reduction residue. Results strongly supported the feasibility of Fe_2O_3 reduction by lignite and obtaining pure CO_2 from the off-gases. Fe_2O_3 can be fully converted to Fe_3O_4 by pyrolysis and gasification intermediates primarily H_2 and CO, which was confirmed by both the off-gas concentrations and X-ray diffractometer analysis. A 0.75 g portion of Fe_2O_3 can be completely reduced to Fe_3O_4 by the volatile matter released from 0.1 g coal, and Fe_2O_3 can be fully reduced to Fe_3O_4 by steam char gasification products provided that the molar ratio of carbon in char to Fe_2O_3 is 1:6. The purity of CO_2 in the outlet gases was higher than 85% when Fe_2O_3 was reduced by intermediate products during coal pyrolysis, and the purity of CO_2 in the off-gases was higher than 95% when Fe_2O_3 was reduced by intermediate products resulting from steam char gasification, making CO_2 sequestration disposal desirable for high purity CO_2. The char gasification reaction rate was slow compared with the reactivity of the iron oxide with the char gasified intermediates, indicating that char gasification was the rate-limiting step in the reduction process. In the steam char gasification process, the times it took to reach 90% carbon conversion for K-10-char and Ca-10-char were 15 and 30 min, respectively, at 1123 K, but the time for the raw char was 50 min at 1173 K.

1. Introduction

It is well-known that CO_2 together with other greenhouse gases has likely caused an increase in global temperature.[1] A reduction in emissions of greenhouse gases, in particular CO_2, is pressing.[1–3] The worldwide fossil-fuel-based power generation sector produces about one-third of the overall anthropogenic CO_2 emissions;[4] therefore, there is an urgent requirement to sequester CO_2 from the combustion of coal. In a conventional combustion system, fuel is directly mixed with air and burned, resulting into a low concentration of CO_2 in the presence of a majority of nitrogen. Disposing of the diluted CO_2 emissions creates a significant energy penalty. For a coal-fired power plant, roughly one-fifth of the electricity produced will be lost to CO_2 separation and compression because of its low concentrations in flue gases.[1] The estimated cost of the CO_2 disposal, ~$4/ton of carbon,[5] is much smaller when compared with the cost of separating CO_2 from typical flue gases, which is typically in
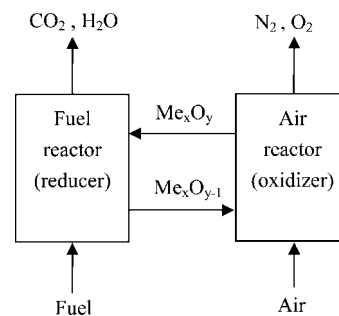

Figure 1. Schematic diagram of the CLC process.

the range of $100–200 U.S./ton of carbon,[5] making CO_2 disposal desirable only if high concentration CO_2 is available.

Among available or proposed techniques involving CO_2 separation in the combustion process, chemical-looping combustion (CLC) is one of the promising techniques to obtain pure CO_2 from a power plant in situ allowing for CO_2 sequestration.[5,6] The CLC process including a fuel reactor and an air reactor is shown in Figure 1. In CLC, fuel and oxygen are contacted via an intermediate oxygen carrier that is alternately oxidized and reduced, and the oxygen carrier solids are circulated between the fuel reactor and the air reactor. In the fuel reactor, the metal oxide (Me_xO_y) reacts with the fuel to form CO_2, H_2O, and the reduced metal oxide (Me_xO_{y-1}). In the air reactor, the reduced metal oxide (Me_xO_{y-1}) is oxidized by air to form metal oxide (Me_xO_y). The main advantage of CLC compared to the

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* Corresponding author. Tel./fax: 86-10-62789955. E-mail: cains@tsinghua.edu.cn.

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conventional combustion is that CO_2 is inherently separated without nitrogen dilution. The majority of studies about CLC has focused on gaseous fuels such as methane, natural gas, and syngas.[7–18] However, the natural gas supply cannot fully support the energy demand for the long term.[19,20] Solid fuels are considerably more abundant than gaseous fuels;[19,20] therefore, the adaptation of CLC to solid fuels would be highly attractive.

Systems with interconnected fluidized bed reactors (IFBRs)[5,21] and a circulating fluidized bed (CFB) with a combination of several loop seals[19] have been proposed for CLC. However, the main drawbacks of these reactor concepts are due to the transport of the oxygen carrier. Not only is an additional energy input required to transport the particles, but a cyclone is also required to separate the particles from the hot flue gas stream. This particle separation is particularly difficult to perform due to the high temperature and pressure and the fact that fines need to be removed to protect the downstream gas turbine. For a solid-fuels-fueled CLC process, the solid fuel can be directly introduced to the fuel reactor in the FBR system.

A packed bed reactor (PBR) concept for CLC is proposed by Noorman et al.[22] where the oxygen carrier solids are stationary and are alternately exposed to a reducing and oxidizing atmosphere via periodic switching of the gas feed streams. The main advantages of this PBR concept are that the separation of gas and particles is intrinsically avoided and the reactor can be much more compact. Another important difference between PBR and FBR is that, in a packed bed reactor, the oxidation conversion of the oxygen carrier is complete, whereas, in an FBR, only a part of the oxygen carrier's oxidation conversion is utilized.[21] In order to achieve high energy efficiency, a continuous high temperature gas stream supply to the gas turbine is required. This can be achieved with packed bed operation by at least two parallel fixed-bed reactors operated in a cyclic manner, which was proposed by Li et al.[23] When a fixed bed or a packed bed reactor is used for solid-fuel-fueled CLC, coal gasification and CLC would be performed separately. It is well-known that the coal gasification technology for syngas production is mature. A system including two parallel fixed bed reactors for CLC with syngas and an external coal gasification process is another option for solid-fuel-fueled CLC. However, coal-fueled CLC is a new technology for clean coal technology. A lot of work needs to be carried out in oxygen carrier characteristics, reaction kinetics, hydrodynamics, and so on for the design and operation conditions of a CLC system.

One means of performing CLC with solid fuel is that metal oxide is reduced by a syngas, consisting primarily of CO and H_2, which is obtained by first gasifying the coal. A new type of coal-gas-fueled CLC is proposed by Jin et al. where the clean coal gas produced from the gasifier in an integrated gasification combined cycle (IGCC) power plant is fed to a chemical-looping combustor.[24] In this system, CO_2 removal equipment is not required, such that an additional gain in 5–10% in the overall energy efficiency of power generation can be achieved compared to the conventional IGCC with CO_2 recovery.[24] Another method is to introduce coal directly into the fuel reactor in CLC where the metal oxide is reduced by the solid fuel.[25–29] When coal and the oxygen carrier are mixed, the oxygen carrier can be reduced to a metal or a reduced metal oxide either in an indirect path by pyrolysis and gasification products of solid fuels or in a direct way by solid fuels under an N_2 atmosphere for both CuO[25] and Fe_2O_3[26] systems in thermogravimetric analysis. However, the proportion of oxygen carrier reduced by pyrolysis products and char, respectively, can not be distinguished because the oxygen carrier reduction by volatile matter and char occurs simultaneously, which is an obstacle for the design of the reactor.

Leion et al. performed iron oxide reduction–oxidation experiments with a fluidized bed reactor using petroleum coke and suggested that the gasification rate was slow compared with both the reaction rate of the gasified products with the iron oxide

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Table 1. Proximate and Ultimate Analysis of Coal Sample

	proximate analysis (wt %, ad basis)				ultimate analysis (wt %, ad basis)				
sample	inherent moisture M	ash A	volatile matter VM	fixed carbon FC	C	H	N	S	O (diff)
BL	3.89	10.89	37.31	47.91	63.09	4.17	0.96	0.33	31.45

and the oxidation rate of reduced iron oxide with oxygen, thus gasification was the time-limiting step in CLC.[27] The time it took to reach 95% carbon conversion at 1123, 1223, and 1273 K were 76.8, 14.8, and 10.6 min, respectively, under 50% steam.[27] It is concluded by Leion et al. that a temperature of 1123 K gave a larger proportion of carbon that has only been converted to CO due to the most likely reason of the slower reaction of iron oxide with CO.[27] However, there are some other oxygen carriers which show high reactivity with CO at 1123 K and temperatures lower than 1123 K;[17,18] for the iron-based particles, the time to reach complete conversion under 40 vol % CO and 20 vol % CO_2 at 973−1123 K is shorter than 30 s.[17]

Dennis et al. have confirmed the feasibility of using steam and CO_2 to gasify lignite in the presence of iron oxide, but more investigation needs to be carried out to clarify the composition and morphological features of the oxygen carrier.[28,29] On the other hand, the reaction conditions need to be optimized to obtain high purity CO_2. Results from the publications indicate that solid fuels with high volatile matter and high reactivity of the char produced would be considerably desirable for CLC processes.[25,28,29]

One of the purposes of this study is to reveal the proportion of oxygen carrier reduced by coal pyrolysis intermediate products and gasification intermediate products, respectively, by using a fixed bed reactor as a simulating reactor. Another objective in the present study is to obtain some preliminary results of the effect of alkali and alkaline earth metal on the gasification of char in the presence of oxygen carrier in order to make clear the extent of the gasification temperature lowered by the catalyst. The potential purity of CO_2 from CLC using coal as a fuel which has been investigated inadequately is strengthened in this study. In the meantime, the morphology and chemical properties of the oxygen carrier particles were characterized using an X-ray diffractometer (XRD) and a scanning electron microscope (SEM) to support the reduction mechanism of the oxygen carrier.

2. Experimental Section

2.1. Preparation of Test Samples. The oxygen carrier was prepared from Fe_2O_3 powder from the manufacturer Shantou Xilong Chemical Factory, China, with a purity of 99.9%. The received Fe_2O_3 particles were sieved to a size range of 200–450 μm. The particles of Fe_2O_3 were then placed in a furnace, heated to 1173 K, and maintained at this temperature for 5 h. The calcined particles were then sieved into a size fraction of 200–450 μm. The BET areas of the Fe_2O_3 particles as received and the calcined Fe_2O_3 particles are 2.64 and 1.35 m²/g, respectively, as determined by a Micromeritics micropore analyzer, ASAP2010. The calcined Fe_2O_3 was used as the fresh oxygen carrier in this study.

A Chinese low rank coal, Baorixile lignite (BL) from an opencast mine, and the chars produced from the lignite were used as solid fuel. The proximate and ultimate analyses of the parent coal are listed in Table 1. Coal samples were sieved to a size range of 200–450 μm. The removal of mineral matter from coal by acid treatment (demineralization) is accompanied by structural changes,

which alters the nature and, thus, the behavior during gasification.[30,31] Therefore, in this study, the catalyst was added to the raw coal directly (without destructive pretreatment) by impregnation with the following procedure: analytical grade anhydrous K_2CO_3 (from Beijing Chemical Factory, China) and $Ca(NO_3)_2 \cdot 4H_2O$ (from Shantou Xilong Chemical Factory, China) were employed as the precursors for catalyst, coal (10 g) was added to 30 mL aqueous solutions of the above salts, the slurry was stirred for 3 h at ambient temperature and dried in air overnight at 378 K. The catalyst loading was 10% in terms of the mass ratio of metal to coal.

The chars were prepared as follows, all samples were devolatilized in the fixed bed reactor shown in Figure 2 under the flow rate of 300 mL/min Ar with a purity of 99.995% at a heating rate of 30 K/min from room temperature to a final temperature of 1173 K, and the soaking time was 30 min. The reactivity of a char is known to be influenced by its heating treatment history,[28,29] but the reactivity of a char hardly changes under a temperature of 1173 K from published results[32,33] and preliminary results obtained in the present study. Hence, this method of preparing the chars is sufficient for the measurements of the reactivity of the chars.[28,29] The chars produced from the parent coal and coal loaded with K and Ca are denoted as raw char, K-10-char, and Ca-10-char, respectively, and their ultimate analyses are given in Table 2.

2.2. Experimental Setup. The chemical-looping combustion of coal with Fe_2O_3 was carried out under atmospheric pressure using the fixed bed apparatus as shown in Figure 2.

The fixed bed reactor consists of an outer stainless tube and an inner quartz tube which has a length of 700 mm and an inner diameter of 10 mm. A fixed bed of quartz frit is located at 325 mm from the bottom of the quartz tube. The flow rate of carrier argon is controlled by a mass flowmeter. The purity of Ar in this study is always 99.995%. The reactor was heated by an electric furnace. The bed temperature was monitored by a K-type thermocouple. The distilled water was introduced from the top of the reactor by a pump (2PB10C, China Spacesat Co., Ltd.). The high temperature steam was generated by forcing water through an evaporator section containing 50 mm of quartz sand as shown in Figure 2b to guarantee the completed evaporation of the water. On the other hand, the pressure measured by a pressure gauge linking to the fixed bed reactor was stable. More details about the fixed bed reactor system can be found in the earlier published paper.[23] A continuous flow of steam was guaranteed in this study. The high temperature steam passed through the fixed bed and was then allowed to flow through the bottom of the reactor to a cooling section which was made of stainless tube coil; at last, steam was condensed back to water and separated from product gases by a liquid/gas separator.

The gases after the liquid/gas separator were led to a gas analyzer TCD-GC (Perkin-Elmer, Auto System XL) where the concentrations of H_2, CO, CH_4, and CO_2 were measured. The gas concentrations analyzed in this study have excluded the steam. The off-gases of H_2, CO, CO_2, and CH_4 were sampled every 3 min by GC.

The influence of pyrolysis intermediate products, steam char gasification products, and the catalytic effect of K and Ca on the

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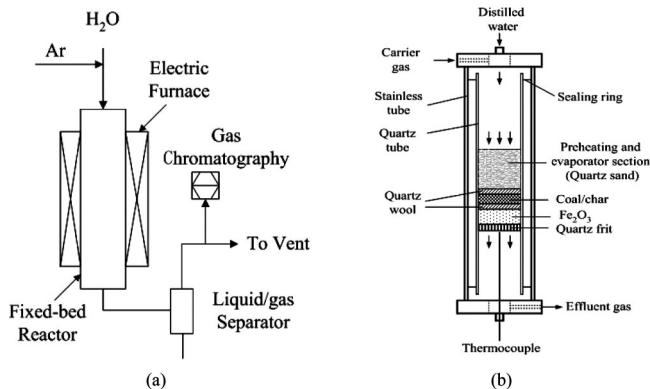
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Figure 2. Schematic diagram of the reaction system (a) and details of the fixed bed reactor (b).

Table 2. Ultimate Analysis of Char Samples (wt %, ad basis)

samples	C	H	N	O, S (by diff)
raw char	74.87	0.42	0.65	24.06
K-10-char	62.57	0	1.07	36.36
Ca-10-char	60.62	0	1.19	38.19

reduction of Fe_2O_3 and product gas concentration profiles were evaluated by the fixed bed reactor. The coal/char and Fe_2O_3 were packed in the fixed bed with the form as shown in Figure 2b. The experiments using a mixture of coal and iron oxide particles are not carried out because the main purpose in this study is to reveal the proportion of iron oxide reduced by coal pyrolysis intermediate products and gasification intermediate products, respectively. Under real conditions, recycled CO_2 is an option for the gasifying agent. It is desired to use a mixture of CO_2 and steam (ratio of H_2O/CO_2 may be varying) as a gasifying agent for economical reasons.[27] It is well-known that steam reacts faster with char than CO_2 does,[34] and therefore, the steam would normally be expected to be the referred gasifying agent. In the CLC process, generally, the oxygen carrier is alternately exposed to air and fuel streams. Generally, the oxidizing rate of the oxygen carrier was considerably faster than the rate of the reducing reaction[8] and it was found in the published experimental results that iron oxides supported on several inerts such as Al_2O_3, SiO_2, yttria-stabilized zirconium, and TiO_2 had high reactivity and good reaction stability over multiple reduction–oxidation cycles,[18] indicating that more attention should be paid to the reduction of iron oxide. Therefore, this study focuses on the reduction process of iron oxide.

The reduction of Fe_2O_3 by coal or char was carried out by three test series. In series I, Fe_2O_3 was reduced by coal pyrolysis intermediate products. In this series, the mass of Fe_2O_3 was changed, and the mass of coal was maintained at about 0.2 g. The sample was heated under an Ar atmosphere from room temperature to 1173 K. After 5 min of soaking time, the electric furnace was turned off to cool the reactor quickly. In series II, Fe_2O_3 was reduced by the steam gasification products of raw char, K-10-char, and Ca-10-char. The sample was heated under an Ar atmosphere to a set temperature, and the water was introduced to the reactor when the temperature was stabilized at the set temperature. In series III, Fe_2O_3 was reduced by coal pyrolysis products and sequential nascent char steam gasification products in situ. The sample was heated under Ar atmosphere to 1173 K, and the water was introduced to start the steam gasification when the temperature was stabilized at 1173 K. Each set of experiments was repeated at least three times to guarantee the reliability of the data obtained. The flow rates of Ar and water were maintained at 100 mL/min and 0.05 g/min, respectively, and the heating rate is always 30 K/min in this study. The amounts of the samples used in each set of experiment are discussed in the relevant sections.

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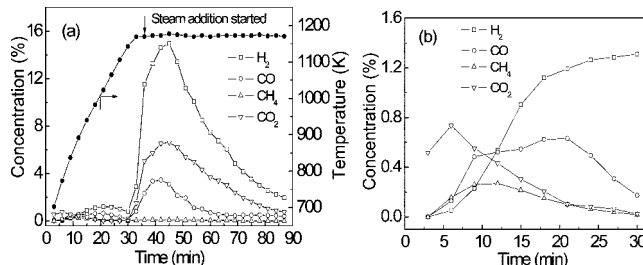

Figure 3. Gas concentrations during coal pyrolysis and steam gasification without Fe_2O_3. The mass of coal was 0.205 g. The flow rates of Ar and water were 100 mL/min and 0.05 g/min, respectively.

2.3. Data Evaluation. The actual concentrations of H_2, CO, CO_2, and CH_4 in the outlet gases are measured by the GC, and the actual concentration of Ar in the outlet gas can be calculated. The Ar flow (known by a mass flowmeter) is divided by the concentration of Ar to obtain the total flow of the off-gases. The total flow of the off-gases is multiplied by the concentrations of H_2, CO, CO_2, and CH_4 to get the flow of H_2, CO, CO_2, and CH_4. Then the mass of CO, CO_2, and CH_4 converted up until the time t are calculated by integration using the Simpson method, and the total amount of carbon in the outlet gases can be obtained. At last, the total mass of carbon in the outlet gases is divided by the total amount of carbon in the original coal or char to get the carbon conversion X as follows[27,33]

$$X = \frac{m_{CO} + m_{CO_2} + m_{CH_4}}{m_{total}} \quad (1)$$

where m_{total} is the total amount of carbon in the original coal or char; m_{CO}, m_{CO_2}, and m_{CH_4} are the mass of carbon in the products CO, CO_2, and CH_4 converted up until the time t; and t is the time elapsed since the start of the reducing period.

Now the gasification rate R is calculated using eq 2 based on the carbon conversion X

$$r = \frac{1}{1-X} \frac{dX}{dt} \quad (2)$$

2.4. XRD and SEM Analysis. An X-ray diffractometer (Bruker D8 advance) using Cu Kα radiation (40 kV, 40 mA) was used to analyze each of the iron oxide samples. The samples were scanned in a step-scan mode with a step size of 0.02° over the angular 2θ range of 10−80°.

The morphological features of iron oxide samples were characterized by a scanning electron microscope (SEM, KYKY-2000). The electron beam energy was 20 kV. In most cases, two magnifications at 150×, 300×, and 5000× were selected to be analyzed.

3. Results and Discussion

3.1. Gas Concentrations Profiles during Coal Pyrolysis and Steam Char Gasification without Fe_2O_3. Figure 3 shows the actual gas concentrations in the outlet gases as a function of time during coal pyrolysis and char steam gasification without Fe_2O_3. The portion of the gas concentrations during coal pyrolysis are enlarged in Figure 3b. Pyrolysis began at 641 K corresponding to time zero in Figure 3, and the water was introduced and steam char gasification began at 33 min when the temperature stabilized at 1173 K. The initial peak of CO_2 at 773 K is due to the devolatilization of the coal. It is found that CO_2 decreases and becomes zero at 1000 K during pyrolysis; after that, CO_2 increases evidently when the steam is introduced and reaches another maximum concentration. H_2 increases with temperature during pyrolysis and increases sharply to another peak when the steam is introduced. CH_4 reaches a maximum concentration at about 850 K during
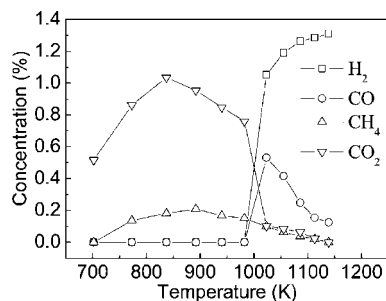
Figure 4. Gas concentrations during the reduction of Fe_2O_3 by coal pyrolysis intermediates. The masses of coal and Fe_2O_3 are 0.208 and 0.502 g, respectively.
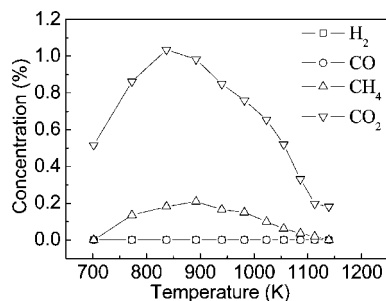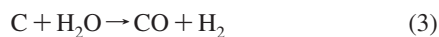

Figure 5. Gas concentrations during the reduction of Fe_2O_3 by pyrolysis intermediates. The masses of coal and Fe_2O_3 are 0.206 and 1.500 g, respectively.

pyrolysis and becomes almost zero in steam char gasification. There are two peaks of CO during pyrolysis at 850 and 1050 K, respectively. H_2, CO_2, and CO reach their maximum concentrations simultaneously during the steam char gasification stage.

In the steam char gasification process, when the iron oxide is not present, H_2 can only be produced either by gasifying the char with steam in reaction 3 or by the water−gas shift (WGS), reaction 4. This argument neglects the hydrogen contained in the char because the char had a molecular formula of $CH_{0.08}N_{0.05}$ based on the ultimate analysis. CO_2 produced from reaction 4 might react with the char in reaction 5. The stoichiometry of these reactions is such that the rate of H_2 production is equal to the rate of production of CO plus twice the rate of CO_2 production. The values of the gas concentrations shown in Figure 3 verify this relationship. The fact that large concentrations of CO_2 are produced indicates that the WGS reaction is important in this system.[29]

$$C + H_2O \rightarrow CO + H_2 \quad (3)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (4)$$

$$C + CO_2 \rightarrow 2CO \quad (5)$$

3.2. Fe_2O_3 Reduction by Coal Pyrolysis Intermediates. The outlet gas concentrations as a function of temperature during pyrolysis are shown in Figure 4. Before 1000 K, the H_2 and CO released during pyrolysis were fully oxidized to CO_2 and H_2O. It is shown in Figure 5 that when the mass of Fe_2O_3 is larger than 1.5 g, the gases are almost CO_2 and CH_4. It is suggested that CO and H_2 released during pyrolysis are completely oxidized by Fe_2O_3 even though the temperature is

between 700 and 1000 K. The gas concentrations in the case of 2.050 g Fe_2O_3 and 0.206 g coal are identical to the case as shown in Figure 5. By comparing Figure 3 with Figure 5, it is found that CO and H_2 are completely oxidized by Fe_2O_3 resulting in the purity of CO_2 being higher than 85% on an Ar-free basis, making clear the fact that the reactivity of Fe_2O_3 with syngas is higher than that with methane.[13]

An earlier investigation by Mattisson et al. showed a high increase in reduction rate for Fe_2O_3 and CH_4 with increasing temperature.[8] However, Fe_2O_3 failed to oxidize the CH_4 released during pyrolysis as shown in Figures 4 and 5. The reason that Fe_2O_3 failed to oxidize the CH_4 released during pyrolysis was due to the low temperature in the present study because the CH_4 peak occurred at about 850 K. After 20 min corresponding to 1000 K, CH_4 disappears due to the gradual completion of CH_4 evolution during pyrolysis and the oxidation of CH_4 by Fe_2O_3. Some published experimental results indicated that CH_4 could be fully oxidized to CO_2 and H_2O at 1173[14] and 1223 K.[11] In industrial facilities with fast heating rate and high temperature, CH_4 is expected to be fully oxidized by oxygen carrier to CO_2 and H_2O. After calculation, the amount of CH_4 evolved from 0.208 g coal during pyrolysis is 1.3×10^{-4} mol based on the results in Figure 4. According to a specific reaction, the amount of iron oxide needed to fully convert the evolved CH_4 can be calculated.

A breakthrough is observed at 1000 K due to the complete reduction of Fe_2O_3 shown in Figure 4. In a fixed bed, the reacting gases go through a Fe_3O_4 layer before they react with fresh Fe_2O_3. Syngas reacts with iron oxide in a transition zone.[35] The length of the transition zone in the iron oxide bed could be used to know the iron oxide inventory needed to convert a determined flow of gasified gases.[35] However, there are some difficulties in calculating the reacting zone for the gas concentrations resulting from pyrolysis change, and the tarry material is unknown at present. It is necessary to use a fixed concentration of syngas to conduct the reduction of Fe_2O_3 in future work in order to obtain the transition zone data for the design of the industrial reactor.[35]

The 2θ angles and relative intensity of Fe_2O_3, Fe_3O_4, FeO, and Fe from the XRD library are listed in Table 3 to distinguish different Fe species in the iron oxide sample. Figure 6 shows the XRD spectra of pure Fe_2O_3 and its residue after reduction by coal pyrolysis intermediates where the discrete vertical lines in Figure 6a and b are the standard spectra of Fe_2O_3 and Fe_3O_4, respectively. There are no peaks found either at 36.1° and 41.9° or at 44.7° and 65.0° in Figure 6, which indicates that there is no FeO or Fe. There are no peaks found at 33.4° and 35.8° in Figure 6b, giving clear evidence that Fe_2O_3 was completely reduced to Fe_3O_4 by pyrolysis intermediate products when the mass of Fe_2O_3 was lower than 1.5 g and the mass of coal was maintained at 0.2 g. On the other hand, in the case of 0.206 g coal and 1.500 g Fe_2O_3, the mass loss of iron oxide is 3% by weight after the experiment, indicating that Fe_2O_3 is fully reduced to Fe_3O_4.[11] Excluding the mass of iron oxide reduced by the tarry material during pyrolysis, the minimum mass of Fe_2O_3 to fully convert the gases CO and H_2 evolved from 0.205 g coal to CO_2 and H_2O during pyrolysis is 1.152 g based on the calculation method mentioned in section 2.3 and the results in Figure 3. Therefore, in this study, the tarry material evolved

Table 3. XRD Spectral Data of Fe Species from the XRD Library

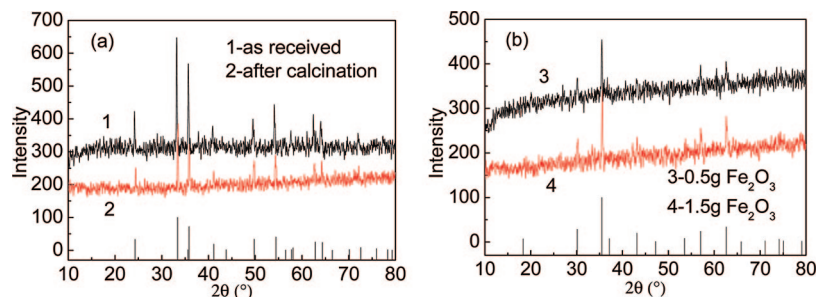| species	Fe_2O_3			Fe_3O_4				FeO			Fe	
2θ (deg)	33.4	35.8	54.5	30.1	35.5	57.0	62.6	36.1	41.9	60.7	44.7	65.0
relative intensity (%)	100	72	40	29	100	24	34	67	100	46	100	20

Figure 6. XRD characterization of iron oxide: (a) pure Fe_2O_3, (b) Fe_2O_3 reduced by pyrolysis intermediates.
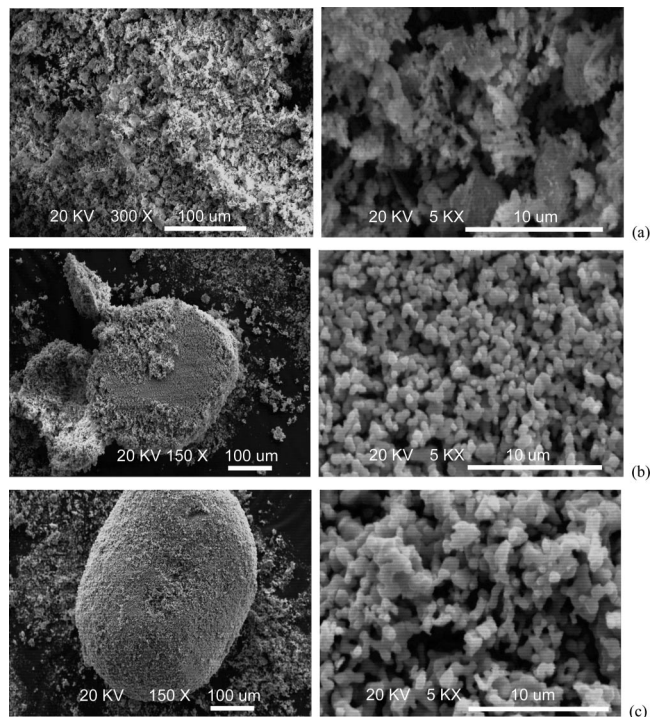

Figure 7. SEM images of Fe_2O_3 under different treatment: (a) Fe_2O_3 powder as received, (b) Fe_2O_3 particle after calcination at 1173 K for 5 h, (c) reduction residue of Fe_2O_3 from the 0.502 g Fe_2O_3 which was reduced by pyrolysis intermediates released from 0.208 g coal.

Figure 8. Pore size distribution of the tested iron oxide samples.

Figure 9. Gas concentrations during the reduction of Fe_2O_3 by raw char steam gasification products. The masses of char and Fe_2O_3 are 0.071 and 3.59 g, respectively.

from 0.205 g coal during pyrolysis can reduce about 0.35 g Fe_2O_3 to Fe_3O_4 by coarse estimation based on the experimental results with the fact that 1.5 g Fe_2O_3 can be fully reduced to Fe_3O_4 by the pyrolysis intermediates from 0.2 g coal.

SEM images of Fe_2O_3 under different treatments with two magnifications for each sample are shown in Figure 7 where the images in the left side are in a lower magnification scale. Pure Fe_2O_3 powder as received has a rough surface and looks like flock as shown in Figure 7a. The surface structure and morphology of pure Fe_2O_3 particles varied after calcination. Figure 7b shows that the calcined Fe_2O_3 particle consists of small granular surfaces and grains of about $1-3$ μm in size, but the XRD spectra of Fe_2O_3 hardly change after calcination when compared with that of Fe_2O_3 as received as shown in Figure 6a. Some melted spots were observed when Fe_2O_3 particles were reduced by pyrolysis intermediates as shown in Figure 7c, but these were not severe. This was further supported by the BET areas and pore size distribution information. The specific surface areas of the calcined Fe_2O_3 and reduced Fe_2O_3 are 1.35 and 1.25 m^2/g, respectively. Figure 8 shows the pore
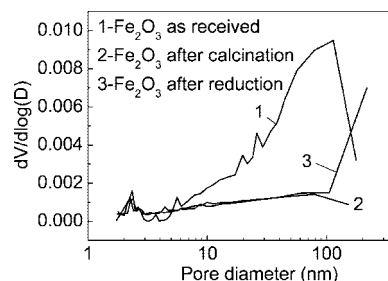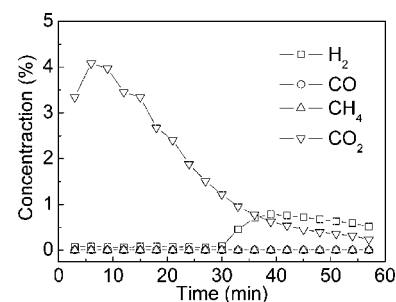
size distribution of the different iron oxide samples. After calcination, the average pore diameter of Fe_2O_3 particles decreases. The pore distribution of the calcined Fe_2O_3 is almost identical to that of the reduced Fe_2O_3 in the size range of 2–80 nm. But, after reduction, the average pore diameter becomes larger compared with that of the calcined Fe_2O_3 particles because the portion of the pore larger than 80 nm increases. Despite the fact that the present Fe_2O_3 was not optimized, it was able to oxidize almost all of the H_2 and CO produced from coal. In order to avoid a high rate of sintering, it may be advantageous to manufacture synthetic iron oxide particles incorporated in a carrier support and binder which may also improve the reactivity, durability, and longevity of the oxygen carrier particles.[9,14,17,18]

3.3. Fe_2O_3 Reduction by Steam Char Gasification Intermediate Products. The gasification temperature for the raw char is 1173 K and that for K-10-char and Ca-10-char is 1123 K. Figure 9 shows the gas concentrations as a function of reducing time for Fe_2O_3 reduction by raw char steam gasification products at 1173 K. The gasification products were fully oxidized to CO_2 and H_2O before 30 min as shown in Figure 9 resulting into a CO_2 stream with almost 100% purity. At 30 min, 80% carbon in the char was converted to CO_2. It was suggested from Figure 9 that the purity of CO_2 on an Ar-free basis was higher than 95% if the mole ratio of carbon to Fe_2O_3 was optimized.

(35) Adánez, J.; Abad, A.; García-Labiano, F.; de Diego, L. F.; Gayán, P. H_2S Retention with Ca-Based Sorbents in a Pressurized Fixed-Bed Reactor: Application to Moving-Bed Design. *Fuel* **2005**, *84* (5), 533–542.
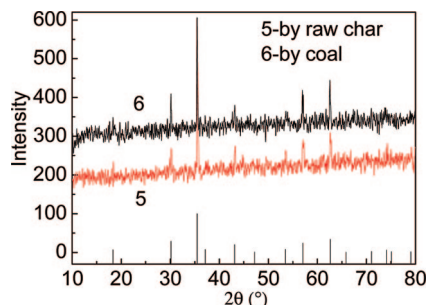
Figure 10. X-ray diffraction spectra of reduced Fe_2O_3 residue by raw char steam gasification products and coal reaction products.

Fe_2O_3 was assumed to be fully reduced to Fe_3O_4, which was approved by XRD analysis shown in Figure 10 where the discrete vertical lines were the standard spectra of Fe_3O_4. There are no peaks for FeO and Fe based on the 2θ angles listed in Table 3. The conclusion that Fe_2O_3 forms only Fe_3O_4 rather than FeO or Fe can be justified by the following thermodynamics analysis. For the following reaction

$$0.788CO + 0.947Fe_3O_4 \rightarrow 0.788CO_2 + 3Fe_{0.947}O \quad (6)$$
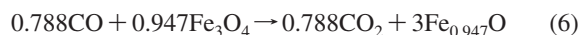
the equilibrium constant can be calculated from the standard Gibbs free energy changes. The equilibrium constant of reaction 6 $K_p = (p_{CO_2}/p_{CO})^{0.788} = 1.749$ (calculations based on the data from NASA Glenn thermodynamic coefficients[36]) at 1173 K. Therefore, for the Fe_3O_4 to be reduced to FeO at 1173 K would require $p_{CO}/p_{CO_2} > 0.49$, which it was not by judging from the results in Figure 9. Similarly, for reaction of Fe_3O_4 with H_2
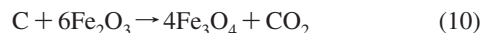
$$0.788H_2 + 0.947Fe_3O_4 \rightarrow 0.788H_2O + 3Fe_{0.947}O \quad (7)$$
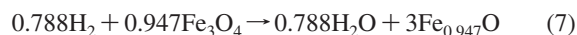
For the Fe_3O_4 to be reduced to FeO at equilibrium at 1173 K, $p_{H_2}/p_{H_2O} > 0.39$ would be required, which was not the case because the H_2 concentration is lower than 1% and the steam concentration is about 38% in the iron oxide bed. As shown in Figure 9, after 30 min, the products were almost H_2 and CO_2, indicating that the WGS reaction is important. It is suggested by Abad et al. that steam concentration affects the reduction mechanism of Fe_2O_3 with H_2; furthermore, the solid inventory is affected by the steam concentration due to the WGS reaction.[17]

If it is assumed that Fe_2O_3 is reduced to Fe_3O_4 in reactions 8 and 9 as follows,

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O \quad (8)$$

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \quad (9)$$
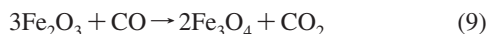
the overall reaction is

$$C + 6Fe_2O_3 \rightarrow 4Fe_3O_4 + CO_2 \quad (10)$$

The molar ratio of Fe_2O_3 to carbon is 6 in the overall reduction reaction 10.[28,29] Therefore, the theoretical capacity of 3.59 g Fe_2O_3 is 0.0037 mol of carbon corresponding to 0.060 g raw char, indicating that the carbon is excessive in the case of 3.59 g Fe_2O_3 and 0.071 g char where the molar ratio of Fe_2O_3 to carbon in the char was 5. For the reduction of Fe_2O_3 with CO (reaction 9) in the absence of solid carbon, p_{CO_2}/p_{CO} under thermodynamics equilibrium is larger than 10^4 (calculations based on the data from NASA Glenn thermodynamic coefficients[36]) in the temperature range of 673–1473 K, so that 99.999% purity of the
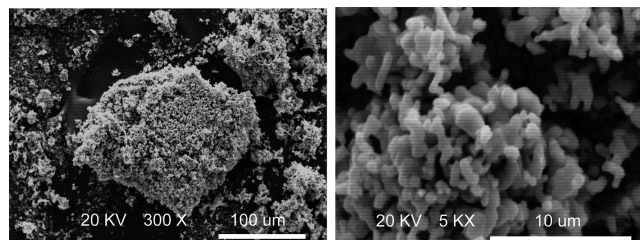
(36) McBride, B. J.; Zehe, M. J.; Gordon, S. *NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species*; Report TP-2002-211556, NASA: Washinton, DC, 2002.

Figure 11. SEM images of Fe_2O_3 particles after reduction by steam raw char gasification products at 1173 K.

CO_2 stream can be obtained. Therefore, the CO_2 purity is determined mainly by kinetics no by thermodynamics.

A breakthrough is observed at 30 min in Figure 9. A 0.043 g portion of the carbon in char was converted to CO_2 until 30 min based on the results from Figure 9. In other words, 3.44 g Fe_2O_3 was converted to Fe_3O_4 based on the stoichiometry of reaction 10. Therefore, at 30 min, 0.15 g Fe_2O_3 was in the transition zone and nonreacted zone, which was about 4 mm in this fixed bed. It is necessary to use a fixed concentration of syngas to conduct the reduction of Fe_2O_3 in future work in order to get the accurate value of the length of reacting zone and nonreacted zone for the design the industrial reactor.[35]

SEM images of Fe_2O_3 particles residue after reduction by steam raw char gasification products are shown in Figure 11. Slight sintering between the grains was observed as shown in Figure 11, but the sintering was more severe than that of Fe_2O_3 particles reduction by pyrolysis intermediates because the gasification temperature was more severe than that during pyrolysis. However, to obtain high energy efficiencies, it is needed to work at high temperature. The solution to avoid agglomeration is to obtain an oxygen carrier that has good thermal stability at high temperature. Metal oxides supported on several inerts such as Al_2O_3, SiO_2, yttria-stabilized zirconium, TiO_2, and $MgAl_2O_4$ have been found to react with sufficiently high rates during successive reduction–oxidation cycles.[9,16,18,37] Besides high reactivity, the oxygen carriers must fulfill other characteristics such as a high resistance to attrition and high mechanical strength for industrial applications.

The gas concentrations in the case of Fe_2O_3 reduction by K-10-char and Ca-10-char steam gasification products are almost identical to those of the case shown in Figure 9. CO and H_2 were completely oxidized by Fe_2O_3 resulting in CO_2 having a purity of larger than 95% on an Ar-free basis. Fe_2O_3 was completely reduced into Fe_3O_4 by K-10-char and Ca-10-char steam gasification products at 1123 K. It was confirmed by XRD spectra which was identical to that of the Fe_2O_3 residue after reduction by steam raw char gasification products as shown in Figure 10.

The preliminary extent of gasification temperature lowered by K and Ca is shown in Figure 12a where the gasification temperature is 1123 K for both Ca-10-char and K-10-char and 1173 K for the raw char. The times it took to reach 90% carbon conversion for K-10-char, Ca-10-char, and raw char were 15, 30, and 50 min, respectively, as shown in Figure 12a. The corresponding gasification rates of raw char, Ca-10-char, and K-10-char are shown in Figure 12b. It is hard to measure accurately the rate at the end of gasification due to the carbon in char goes toward depletion.[27] It was interesting to note that the rates increased with carbon conversion and reached a

(37) Corbella, B. M.; de Diego, L. F.; Garcia-Labiano, F.; Adanez, J.; Palacios, J. M. Characterization and Performance in a Multicycle Test in a Fixed-Bed Reactor of Silica-Supported Copper Oxide as Oxygen Carrier for Chemical-Looping Combustion of Methane. *Energy Fuels* **2006**, *20* (1), 148–154.
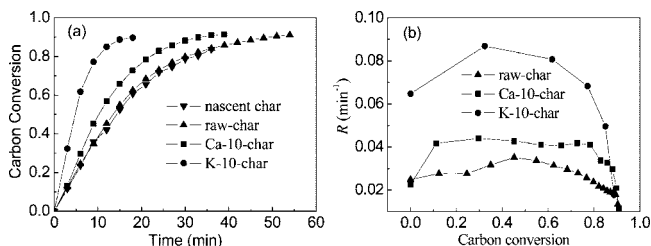
Figure 12. Carbon conversion and gasification rates of raw char, Ca-10-char, and K-10-char. The molar ratio of Fe_2O_3 to carbon is about 6 for the three chars: (▲) 3.59 g Fe_2O_3 and 0.071 g raw char; (■) 3.480 g Fe_2O_3 and 0.075 g Ca-10-char; (•) 3.600 g Fe_2O_3 and 0.066 g K-10-char.
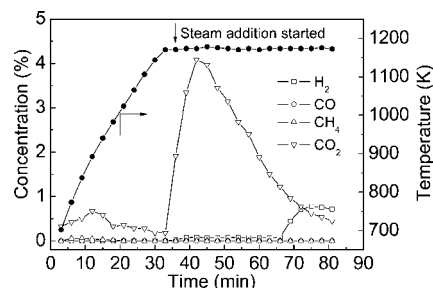

Figure 13. Gas concentrations during the reduction of Fe_2O_3 by both coal pyrolysis and sequential nascent char steam gasification products. The mass of coal and Fe_2O_3 are 0.109 and 4.355 g, respectively.
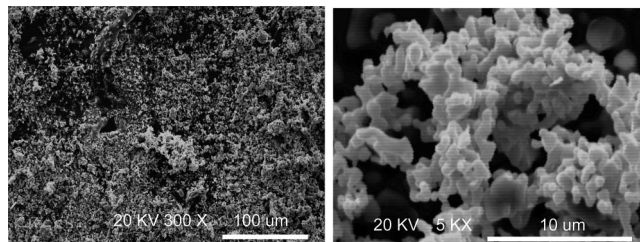

Figure 14. SEM images of Fe_2O_3 particles after reduction by volatile matter and sequential nascent char steam gasification products.

maximum at about 40% carbon conversion, which was also observed by other authors.[38] The gasification rates of Ca-10-char and K-10-char at 1123 K are higher than that of raw char at 1173 K, and the rates of K-10-char are three times of that of the raw char. From preliminary experiments, it was verified that the K and Ca lowered the gasification temperature by 383 and 343 K, respectively. It was suggested that K and Ca can lower the gasification temperature in the presence of oxygen carrier Fe_2O_3 with coal as fuel.

The time for complete gasification of K-10-char which is 15 min in this study is highly beneficial to matching the operation of the air reactor because the complete oxidation time of reduced Fe_2O_3 is about 15 min with 10% O_2 and 1223 K under a fluidized bed reactor.[27] If it is assumed that oxygen carrier and coal are mixed in an interconnected fluidized bed reactor, a fast gasification rate of coal is important for CLC due to the following reasons. When a suitable solids inventory and a suitable circulation rate are established, the conversion level of an oxygen carrier is determined, and complete conversion of syngas and char with oxygen carrier is desired.[21] Generally, the oxidizing rate of the oxygen carrier is much faster than the rate of the reducing reaction, and the volume of the gas flow in the oxidizer is much larger than that in a reducer because a large amount of nitrogen is carried by the air.[19] Then, a fast gasification rate is required in a solid-fuel-fueled CLC system; otherwise, the amounts of unconverted carbon are too large to be transported between the reactors and long residence times (large reactor in scale) are needed for the reduction of the oxygen carrier by syngas and char from solid fuels. So, it is desired to increase the gasification rate for complete conversion of carbon in solid fuels, and then, the reducer will match with the oxidizer considering the solids inventory and circulation rate in industrial applications.

The segregation of the oxygen carrier from unburned carbon and ash is one of the technical problems for the CLC combustion of coal. Furthermore, the addition of K and Ca to coal increases the ash of the coal. If the coal gasification process and reduction of oxygen carrier are separate, the ash separation in a coal gasification process is relatively mature. In the case of a mixture solid fuel and oxygen carrier, the ash with unburned carbon is much lighter than the oxygen carrier in particle density.[19] The oxygen carrier and ash can be separated on the basis of density difference. By controlling the operating velocity in a bubbling fluidized bed, fly ash will be entrained out as proposed by Cao et al.[19] and Leion et al.[27]

3.4. Fe_2O_3 Reduction by Coal Pyrolysis Products and Sequential Nascent Char Steam Gasification Products. The dry gas concentrations during the reduction of Fe_2O_3 by coal

pyrolysis and nascent char steam gasification products in sequence are given in Figure 13. The patterns of gas concentrations in Figure 13 are almost composed by the gas concentrations in Figures 5 and 9.

The minimum mass of Fe_2O_3 needed to fully convert the gases CO and H_2 evolved from 0.2 g coal to CO_2 and H_2O is 8.16 g based on the results from Figure 3. Therefore the volatile matter including tarry material evolved during pyrolysis and gases from char steam gasification from 0.2 g coal can reduce about 8.51 g Fe_2O_3. Preliminary results verified that 0.75 g Fe_2O_3 can be fully reduced to Fe_3O_4 by coal pyrolysis products released from 0.1 g coal and 3.60 g Fe_2O_3 can be completely reduced by the gasification products from 0.06 g raw char. Therefore, 4.36 g Fe_2O_3 was expected to be fully reduced to Fe_3O_4 in theory by coal pyrolysis and char steam gasification products resulting from 0.1 g coal. The corresponding XRD spectra of Fe_2O_3 reduced by coal pyrolysis products and nascent char steam gasification products shown in Figure 10 gave further evidence that Fe_2O_3 was completely reduced to Fe_3O_4.

In all the cases of Fe_2O_3 reduction by char steam gasification products, the content of CO was almost zero, indicating that the WGS reaction was promoted by iron oxide.[29] This is strengthened by the fact that the steam concentration in the reactor is about 38% and the concentration of CO is lower than 4% as shown in Figure 3. As shown in Figure 14, sintering between the grains was observed from SEM images of Fe_2O_3 particles residue after reduction by coal pyrolysis products and nascent char steam gasification products. The degree of sintering is similar to that in Figure 11.

Figure 15 shows the carbon conversions in different cases in sections 3.2, 3.3, and 3.4. In case 1 to case 3, Fe_2O_3 was reduced only by the volatile matter evolved during coal pyrolysis, and it was shown from Figure 15 that the carbon conversion during pyrolysis was lower than 20%. Therefore, char gasification is critical in coal gasification with oxygen carrier. In case 4, steam char gasification started at time zero, and in case 5, nascent char steam gasification started at 33 min. The profile of case 5 in Figure 15 is the cumulative carbon conversion including the carbon converted during pyrolysis. More than 30 min is required for complete gasification of char under 1173 K for cases 4 and

(38) Molina, A.; Mondragon, F. Reactivity of Coal Gasification with Steam and CO_2. *Fuel* **1998**, *77* (15), 1831–1839.
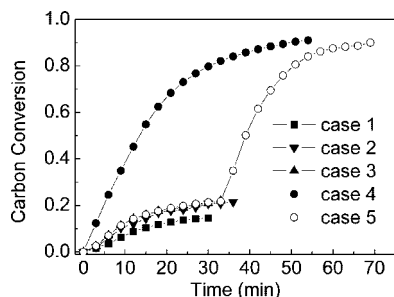
Figure 15. Carbon conversion in the cases of Fe_2O_3 reduction: (case 1) 0.502 g Fe_2O_3 and 0.208 g coal; (case 2) 1.500 g Fe_2O_3 and 0.206 g coal; (case 3) 2.050 g Fe_2O_3 and 0.206 g coal; (case 4) 3.59 g Fe_2O_3 and 0.071 g raw char; (case 5) 4.355 g Fe_2O_3 and 0.109 g coal.

5. However, the gasification intermediate products are fully oxidized by iron oxide even though the reduction time at best is 0.5 s based on the residence time for the gases passing through the iron oxide bed. So, the gasification process is the rate limiting step. The carbon conversion during steam gasification for the nascent char, mass ratio of the carbon produced during steam gasification to the carbon containing in the nascent char at the beginning of steam gasification, is given in Figure 12a. The conversion profiles of the raw char and the nascent char almost overlap as shown in Figure 12a, indicating that the reactivity of the char is not affected significantly by the heating history during char preparation in the present study.

The chemical-looping combustion of coal with iron oxide was carried out under atmospheric pressure in this study. However, the CLC process should be performed at high pressures aiming at increasing the energy efficiency. Furthermore, in a pressurized CLC system, the recovery of the CO_2 requires only a very small amount of additional power for further compression of the CO_2 to pipeline (3.5 MPa) or sequestration pressure (10 MPa).[39] On the other hand, the effect of pressure on the char and the oxygen carrier reactivity is significantly important.

When rate measurements were conducted under conditions where chemical processes alone control the reaction rates, it was found by Roberts et al. that the reaction order of CO_2 and H_2O with char varied from 0.5 to 0.8 at atmospheric pressure and decreased at pressures above approximately 1 MPa.[40] This behavior is explained by Roberts et al. stating that the reason for the shift in reaction order is related to the concentration of adsorbed surface complexes on the char.[40] At atmospheric pressure, the reaction rate is proportional to the number of surface complexes for the surface of the char is not saturated. As the pressure is increased, more surface complexes are produced resulting in an increase in reaction rate. At high enough pressures, the surface will be saturated, such that increases in

pressure will not lead to an increase in the reaction rate. When the gasification rate measurements are investigated under simulated process conditions where significant pore diffusion or product gas inhibitions are important, more attentions should be paid to the effects of total and partial pressure of reactant pressure on the gasification kinetic parameters.

As the pressure is increased, the reaction rate of the oxygen carrier with the gaseous fuel is expected to be increased. However, the experimental results by Garcia-Labiano et al. showed that an increase in total pressure did not lead to an increase in the reaction rate by increasing the partial pressure of the reacting gas; even in some cases, the reaction rate decreased when the total pressure was increased.[39] Therefore, the kinetic parameters necessary to design pressurized CLC systems must be determined at the operating pressure of the industrial system.[39]

The actual reduction reactivity of Fe_2O_3 by coal using a fluidized bed reactor with a high heating rate and good solid mixing should be higher than the reactivity in the fixed bed reactor;[27-29] therefore, the chemical-looping combustion of coal with Fe_2O_3 in fluidized bed reactor is worthy of further investigation.

4. Conclusions

The following conclusions were made from above study:

Oxygen carrier Fe_2O_3 particles can be fully reduced to Fe_3O_4 by coal pyrolysis intermediates and steam char gasification intermediate products, primarily H_2 and CO. A 0.75 g portion of Fe_2O_3 can be completely reduced to Fe_3O_4 by the volatile matter released from 0.1 g coal, and Fe_2O_3 can be fully reduced to Fe_3O_4 by steam char gasification products provided that the molar ratio of carbon in char to Fe_2O_3 is 1:6.

The purity of CO_2 in the outlet gases was higher than 85% when Fe_2O_3 was reduced by intermediate products during coal pyrolysis, and the purity of CO_2 in the off-gases was higher than 95% when Fe_2O_3 was reduced by intermediate products resulting from steam char gasification, making CO_2 sequestration disposal desirable becuase high concentrations of CO_2 were available.

The Fe_2O_3 particles react rapidly with the intermediate products during coal pyrolysis and char gasification products such as H_2 and CO. The char gasification rate is slow compared with the reduction rate of the gasified intermediate products with the metal oxide, thus char gasification is the rate-limiting step in the reduction process.

The gasification rates of Ca-10-char and K-10-char at 1123 K are higher than that of raw char at 1173 K. It is suggested that K and Ca can lower the gasification temperature in the presence of oxygen carrier Fe_2O_3 with coal as fuel.

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