CO₂ gasification of Powder River Basin coal catalyzed by a cost-effective and environmentally friendly iron catalyst

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ABSTRACT

CO₂ gasification of a sub-bituminous Wyodak coal from the Powder River Basin (PRB) was conducted in a fixed-bed laboratory gasifier at atmospheric pressure with FeCO₃ as a catalyst precursor. The effect of iron on the coal pyrolysis was evaluated by thermo-gravimetric analysis (TGA). Scanning electron microscopy (SEM) was employed to characterize the iron performance in the char gasification. The iron species and oxidation states during the coal gasification, characterized by X-ray diffraction (XRD) and Mössbauer spectroscopy, indicate a complex interaction between the reaction atmosphere and temperature, but generally proceed through reduction to FeO

and metallic iron during pyrolysis, followed by subsequent reoxidation to Fe_3O_4 during gasification with CO_2 . The catalytic effect of iron was also quantitatively evaluated by kinetic analysis using shrinking core and random pore models, with the shrinking core model providing superior results. Results show that the apparent activation energy was 92.7 kJ/mol for the untreated coal, which decreased to 58.3 kJ/mol for the coal with 3 wt% Fe. FeCO_3 was shown to have a significant catalytic effect on the Wyodak coal gasification with CO_2 .

Keywords: coal gasification, CO_2 , FeCO_3 , kinetics, catalysis

1. INTRODUCTION

Atmospheric CO_2 concentrations have been increasing and will continue to increase due to the growing demands for energy and the consequent consumption of fossil fuels such as coal, oil, and natural gas [1, 2]. Coal is an abundant, low cost fuel, but with a high ratio of carbon to hydrogen. Control of CO_2 is a major concern for the future use of coal. As the Environmental Protection Agency (EPA) enacts increasingly stringent CO_2 emission regulations, traditional methods of coal combustion are no longer viable as these emit CO_2 above expected regulatory levels [3]. The coal-based integrated gasification combined cycle (IGCC) offers the advantages of higher efficiency in separating CO_2 and other pollutants compared to conventional coal-fired power plants. The CO_2 collected in the IGCC can be injected into oceans or deep underground geological formations [4]. However, the CO_2 from the coal combustion, and water gas shift reaction is usually at a moderately high temperature; discharging the high-temperature CO_2 to the environment wastes not only the material, but also the energy resource.

Gasification is the core of coal-based IGCC systems, and CO₂ can be used as a gasifying agent in coal gasification, as shown in R1

Conventionally, the energy needed to achieve gasification temperature is obtained from exothermic combustion reactions prior to gasification

Using high-temperature CO₂ as a reactant would result in less carbon consumed by coal combustion, thus producing more carbon monoxide in the gasification process. This could create a win-win scenario for environmental protection and the economics of the IGCC.

The hot CO₂ in either unshifted or shifted syngas with characteristics of high pressure and temperature can be separated by using either ceramic or ceramic composite membranes or high temperature pressure-swing based sorbent approaches [5-8]. It should be noted that future gasification technologies will integrate water gas shift reaction into gasification [9]. Therefore, in future gasification technologies, CO₂ capture will very likely be conducted immediately after syngas flows out of the gasifier. The separated CO₂ can then be fed back into the gasifier along with O₂, which reacts with the carbon to generate sufficient heat needed for R1. Additionally, the pressure of the recycled CO₂ at the entrance of gasifier is low and thus a hot gas compressor or a hot gas blower can be used to raise the pressure to the desired level to meet gasification operation requirement [10].

One of the disadvantages of CO₂ gasification is its slow kinetics. Catalytic gasification is one of the main techniques used to improve gasification kinetics due to

its efficiency, availability, and low cost [11-13]. Iron compounds used as coal gasification catalysts have attracted the interest of many researchers because of their abundance, low price, and low environmental impact [13-17]. Asami et al. [15] used iron catalysts precipitated from an aqueous solution of FeCl_3 to catalyze the gasification of brown coal with CO_2 and found that the presence of iron can lower the temperature at which the maximum rate of CO formation occurs by 130-160 K. Suzuki et al. [17] studied the temperature-programmed desorption and pulsed- CO_2 gasification of Yallourn coal char loaded with $\text{Fe}(\text{NO})_3$ and confirmed the following redox cycle by using a $^{13}\text{CO}_2$ pulse

However, the literature contains no reports on FeCO_3 , which exists abundantly in nature as siderite, as a catalyst precursor in CO_2 gasification of coal. Compared to the other iron salts, FeCO_3 is inexpensive and CO_3^{2-} is less harmful than SO_4^{2-} , NO_3^- , and Cl^- to gasification equipment and to the environment [11, 12]. This research was designed to employ FeCO_3 as a precursor in catalytic coal gasification with CO_2 and to investigate the performance of iron on the coal pyrolysis, the associated gasification mechanism, and carbon conversion kinetics.

2. EXPERIMENTS

2.1 Sample Preparation

Raw coal from the Wyoming Powder River Basin, provided by Wyodak Resources Development Corp., was used. Coal particles smaller than 74 μm (passing

through a 200 mesh screen) were used in this work. The specific preparation of the FeCO_3 catalyst has been described in detail elsewhere [11].

The incipient wetness impregnation (IWI) method was used to mix the FeCO_3 with the coal particles [12]. Specific quantities of the iron catalyst were dry mixed with the raw Wyodak coal. Then, an appropriate volume of distilled water was mixed with the Fe-coal mixtures to just wet the surface of the coal. The resulting mixtures were air-dried at 98°C to constant mass and then stored in dark, air-tight receptacles to prevent further changes. The nominal loadings of iron on the coal were calculated on a dry and ash free (DAF) coal basis. A coal sample without catalyst was also prepared adding only distilled water by IWI.

2.2 Sample Characterization

Proximate and ultimate analyses of the raw Wyodak coal were completed, with the results shown in Table 1. The proximate analysis of the raw coal was performed according to ASTM D5142 and D5016, while the ultimate analysis was done using ASTM D5373, D5016, and D4239 methods [12].

Thermo-gravimetric analyses (TGA Instruments SDT Q600) were used to evaluate the mass loss of the samples during pyrolysis. Each sample of approximately 40 mg was loaded on a ceramic capped alumina sample holder and heated at $30^\circ\text{C}/\text{min}$ to 120°C in N_2 at a flow rate of $100\text{ cm}^3/\text{min}$. After 20 minutes of isothermal equilibration at 120°C , the sample was heated at $10^\circ\text{C}/\text{min}$ to final pyrolysis temperatures of 600°C , 750°C , and 900°C , which was the maximum pyrolysis temperature of this study.

X-ray diffraction (XRD) analyses were performed on powdered coal samples in a Rigaku Smartlab X-ray diffraction system using the Cu $K_{\alpha 1}$ line (1.5406 Å) obtained at 40 kV/40 mA, with 2θ ranging from 20° to 80° with 0.020° steps and a dwell time of 0.05 s/step. Scanning electron microscopy (SEM) images were obtained by an FEI Quanta 450 field emission scanning electron microscope with a Schottky field emission gun at an accelerating voltage of 20 kV. Simultaneous energy dispersive X-ray spectroscopy (EDS) was used to analyze the iron distributions in the samples. In brief, Mössbauer spectra were acquired at 295K, 80K, and 4K in Rh on a WEB Research Co. model WT302 spectrometer equipped with a Janus closed cycle He cooling system. Data were collected over a ± 10 mm/s velocity range in 2048 channels with acquisition times ranging from 12h to 6 days, depending on the Fe content of the samples. Spectra were corrected for nonlinearity via interpolation to a linear velocity scale defined by the spectrum of the 25 μ m Fe foil used for calibration, and were fitted using Mexdisd. The details of the Mössbauer spectra experiment are described elsewhere [3]. The samples for XRD, SEM and Mössbauer spectra tests were collected before and after pyrolysis, as well as after 30-minutes of gasification, and after complete gasification (gasification conditions are described in the next section). After pyrolysis or a certain gasification time, the furnace stopped heating and was opened, causing the reactor temperature to decline sharply to 500 °C. Next, air was blown into the furnace to cool the reactor as rapidly as possible, with nitrogen continually introduced into the reactor to keep the sample away from air. When the reactor was at ambient temperature, the sample was collected from the reactor and stored in an airtight vial to protect it from both air and moisture. Nitrogen was also introduced to expel air from the vial.

2.3 Gasification Experiments

All experiments were performed in a fixed-bed reactor at ambient atmospheric pressure, which is approximately 75 kPa at the elevation (~2,200 m) of our laboratory. Figure 1 shows the catalytic gasification apparatus used in this work.

Approximately 5.0 g DAF coal (5.48 g with 0 wt% Fe on dry coal basis; 5.79 g with 3 wt% Fe on a dry coal basis) was used in each test. Initially, N₂ (UHP, US Welding) was introduced into the apparatus to purge the air present in the system. Then, the coal sample was heated at 10°C/min in N₂ with a flow rate of 4.1 cm³/min to the desired gasification temperatures. Gasification was initiated by the introduction of CO₂ (UHP, Praxair) at a flow rate of 180 cm³/min. The CO₂ was heated by the heating tape before flowing into the reactor, and the temperature of CO₂ was monitored by a thermocouple. Mass flow controllers (Porter Instruments Series 201, with a 4 channel PCIM4 controller) were used to control the flow rate of each gas. The stainless steel tubing around the reactor was heat traced to preheat the gas and to prevent coal tar and water condensation at the reactor outlet; the reactor temperatures were monitored by thermocouples. The reactor is a ½" (13 mm) diameter stainless steel tube, and ceramic wool was used to support the coal sample in the reactor. The gasification temperatures (700°C, 800°C, and 900°C) were adjusted in a tubular furnace (Thermolyne 21100) while the pressure of the gasification system was regulated by a back pressure regulator and monitored using pressure gauges. Tar and water in the product gas were separated from the syngas through a water-cooled condenser and collected; the cleaned syngas

was passed through a desiccant-filled water trap for further water removal prior to flow measurement. The syngas was then vented to the fume hood or analyzed by a gas chromatograph (Agilent 3000A micro GC) equipped with two micro-columns (MolSieve 5A PLOT and 4 m PoraPlot U) to separate H₂, CO, N₂, CO₂, and light hydrocarbons such as CH₄, prior to concentration analysis using a calibrated thermal conductivity detector (TCD). All of the collected data were recorded with a data acquisition system.

Figure 1. Schematic diagram of catalytic coal gasification with CO₂ [(1a) N₂, (1b) CO₂, (1c) Ar; (2) mass flow controller; (3) heating tapes; (4) thermocouples and temperature scanner; (5) tube furnace; (6) ceramic wools; (7) coal sample; (8) temperature controller for heating tapes; (9) tar collector; (10) water-cooled condenser; (11) water-trap; (12) micro GC; and (13) data acquisition system].

3 RESULTS AND DISCUSSION

3.1 Coal Characterization

The results of the proximate and ultimate analyses of the raw Wyodak coal are shown in Table 1. As typical of PRB sub-bituminous coals, the as received water content is nearly 20 wt%.

Table 1. Proximate and Ultimate Analyses of the Raw Wyodak Coal.

Proximate Analysis	As Received (wt%)	Moisture Free (wt%)	DAF (wt%)
Moisture	17.81	-	-
Ash	7.17	8.72	-
Volatile matter	36.56	44.48	48.73
Fixed carbon	38.46	46.80	51.27
Total	100.00	100.00	100.00
Ultimate Analysis			
Moisture	17.81	-	-
Hydrogen ¹	2.80	3.40	3.72
Carbon	59.17	71.99	78.87
Nitrogen	0.76	0.93	1.01
Sulfur	0.35	0.43	0.47
Oxygen ¹	11.95	14.54	15.93
Ash	7.16	8.71	-
Total	100.00	100.00	100.00

¹Hydrogen and oxygen values reported do not include hydrogen and oxygen in the free moisture associated with the samples.

3.2 Coal Pyrolysis

Figure 2 shows the results of the TGA analyses of the Wyodak coal and its mixtures with different concentrations of iron during pyrolysis, presented as mass percentages of the residues over the temperature range of 120 – 900°C. The residue percentage increased with concentration of iron between 450°C and 700°C. To clearly describe the iron effect on coal pyrolysis, a plot of sample mass loss rate as a function of temperature is shown as an insert in Figure 2. The mass loss rate is defined as:

$$r = -\left(\frac{1}{W_{daf}} \cdot \frac{dm}{dT}\right) \quad (1)$$

where r is the rate or fractional weight per time, W_{daf} is the initial sample weight on a dry ash- and catalyst-free basis, and m is the instantaneous mass of the sample at temperature T . The mass loss rate was reduced at $\sim 430^\circ\text{C}$ during pyrolysis, while it increased at $\sim 700^\circ\text{C}$ with the addition of iron.

Production of tar and light hydrocarbons is believed to dominate the mass loss during the primary pyrolysis (between 300 and 600°C) [18-20], which indicates the addition of iron decreased the evolution rates of tar and light hydrocarbon at $\sim 430^\circ\text{C}$ during the coal pyrolysis. The effect is enhanced with the increase of iron dosage in the samples.

Figure 2. Thermo gravimetric analysis (TGA) for raw Wyodak coal and the coal with iron [mass of coal: ~ 40 mg; TGA operation conditions [heating rate: $10^\circ\text{C}/\text{min}$ from 120°C to 900°C ; carrier gas and its flow rate: N_2 , $100\text{ cm}^3/\text{min}$].

Figure 3 shows a simplified diagram of the coal pyrolysis process [21]. Tar is believed to be produced by the small coal fragments combining with hydrogen radicals, both of which are formed during thermal cracking of the coal. With the addition of catalyst, hydrogen radicals can be consumed by Fe_2O_3 created from the decomposition of FeCO_3 during the catalyst preparation [11], as indicated below:

Figure 3. A simple diagram of coal pyrolysis process [21]

In the absence of the hydrogen radicals, which are consumed by the iron oxide, a majority of coal fragments are expected to combine and undergo ring condensation processes. This may be the reason that iron reduces the devolatilization rate of coal at $\sim 430^\circ\text{C}$ and the yields of tar and gaseous hydrocarbons, which require hydrogen radicals to form. Another possible reason for the suppressed pyrolysis rates with increasing iron addition is that iron is reportedly octahedrally coordinated to a range of oxygen-containing ligands in coal, including O^{2-} , OH^- , and COO^- [22], which are generally associated with tar precursors. Thus, the devolatilization rate of coal at $\sim 430^\circ\text{C}$ was reduced, while the residue yield increased in the temperature range from ~ 450 to $\sim 700^\circ\text{C}$, compared to the sample without iron. In addition, increasing temperatures would lead to the breakdown of bonds between iron and oxygen-

containing groups. This may explain the second mass loss rate peak at $\sim 680^{\circ}\text{C}$ of Figure 2, as the tar precursors could decompose and be released at the elevated temperature. Figure 2 also shows that iron has little effect on the residue yield when the pyrolysis temperature is above $\sim 720^{\circ}\text{C}$.

Figure 4 presents the XRD results for the samples with 3 wt% Fe pyrolyzed at 600°C and 750°C . When the pyrolysis temperature surpasses 600°C , magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$) begins to be reduced to metallic Fe. By 750°C all magnetite present has been completely reduced to metallic Fe, indicating the reduction of iron oxides took place in this temperature range.

Figure 4. The XRD spectra of the coal samples with 3 wt% Fe after pyrolysis at (a) 600°C and (b) 750°C .

3.3 Coal Char Gasification

When the reactor was at the predetermined temperatures (700 , 800 , or 900°C), CO_2 was introduced into the reactor and reacted with the char obtained from coal

pyrolysis, as shown in R1. The catalytic effect of iron on the char gasification was qualitatively analyzed by the SEM images and quantitatively evaluated by kinetic analysis. To understand the transformation of iron species during the char gasification, the char samples at different gasification times were collected and analyzed by XRD and Mössbauer spectroscopy. The catalytic mechanism of iron on the coal char gasification was analyzed using the XRD and Mössbauer spectroscopy results.

3.3.1 SEM Results

Figure 5. SEM images of the char sample with 3 wt% Fe and 0 wt% Fe after 5 min gasification at 900°C and corresponding distribution of iron atom clusters from EDS: (a) 200 μm scale bar with 3 wt% Fe; (b) 5 μm scale bar for the marked area in Fig. 5(a); (c) 50 μm scale bar with 0 wt% Fe.

Figure 5(a) shows the low magnification (200 μm scale bar) SEM images of the 3 wt% Fe char sample and the distribution of iron atom clusters after 5 minutes of gasification at 900°C. The images show that the catalyst was not distributed uniformly among the coal particles, but concentrated in certain char particles. The non-uniform distribution of iron resulted in a non-uniform distribution of the gasification rate in char samples and low efficiency of the added catalyst. The improvement of catalyst distribution will be studied in future work. To further examine the distribution of the iron, the char particle, as marked in Figure 5(a), and the corresponding iron distribution was amplified to a higher magnification (scale bar of 5 μm) in Figure 5(b).

Compared to the adjacent char particles, the particle with high concentration of iron was eroded substantially, suggesting a significant catalytic effect of iron on the char gasification. Several large (~ 1 μm diameter) lumps formed on the surface of the char particle, which had a high distribution of iron, as indicated in Figure 5(b). Many smaller

(~0.1 μm diameter) lighter colored spheroids also appeared across the particle surface. A possible explanation for these observations is that the active sites formed by iron promoted the consumption of adjacent carbon. As the carbon was gasified, the remaining primary minerals in coal, such as SiO_2 and kaolin, combined together or adjacent to the iron particles to form the smaller spheroids. The small, iron containing spheroids continued to catalyze the gasification, and simultaneously absorbed the primary minerals or combined with other spheroids to increase in size. As the surrounding carbon was consumed by the gasification reaction, the interface of the shrinking, unreacted core receded through the ash, leaving the small spheroids exposed on the particle surface to gradually coalesce.

Figure 5c shows the images of coal particles with 0 wt% Fe obtained under the same gasification conditions as Figure 5a. Compared to Figure 5a, the iron concentration was significantly reduced. Very little iron found by EDS was believed to be derived from the primary mineral in coal. In addition, it is difficult to find a coal particle in Figure 5c the same as the particle shown in Figure 5b. During the pyrolysis and 5 min gasification, the added iron catalyst underwent a reduction and an oxidation process, and was believed to be distributed among the coal particles gradually, as shown in Figure 5a compared to Figure 5c, instead of existing as an independent particle, though the distribution is uneven. Figure 6 shows the EDS result of carbon for the coal particle in Figure 5b. It can be seen that with high iron concentration, some carbon is also found on the particle, as shown in the marked area.

Figure 6. EDS image of carbon for the coal particle in Figure 5b.

3.3.2 Kinetic Analysis

The shrinking core model (SCM) and random pore model (RPM) have often been used to describe the kinetic data collected in coal gasification [23]. The SCM assumes that the gasifying agent is consumed either on the exterior of the coal particle or within the pores close to the particle exterior surface, and then progresses toward the center of the coal particle [24]. The SCM can be expressed as:

$$\frac{dx}{dt} = k_{SC} (1 - x)^m \quad (2)$$

where x is the fractional conversion of carbon at time t , k_{SC} is the specific carbon conversion rate constant, m is a shape factor that depends on the shape of the assumed grains (for spheres, $m = 2/3$; for cylinders, $m = 1/2$; and for flat plates, $m = 0$), which has also been used as the reaction order by some researchers [25, 26].

The RPM takes into account the pore structure of the coal particle and its evolution during gasification. It assumes that the internal surfaces of the pore structure also serve as reaction interfaces and that the cylindrical pores of uneven diameter

enlarge as the internal surfaces erode with the progress of the reaction, eventually merging together [4, 21]. The RPM can be described by the following equation:

$$\frac{dx}{dt} = k_{rp}(1-x)\sqrt{1-\psi \ln(1-x)} \quad (3)$$

where ψ is a dimensionless structural parameter and k_{rp} is the reaction rate constant for the RPM. The RPM can predict the occurrence of the maximal rate during gasification, which exists over the range $2 \leq \psi \leq \infty$ [27, 28], according to the previously mentioned assumption. Kajitani et al. [29] prepared coal chars through a fast heating process ($\sim 450^\circ\text{C/s}$ in a drop tube furnace) and observed that when gasification began, the char surface became rough, causing the appearance of pores, as shown in Figure 6. The RPM was shown to be appropriate under these conditions [29].

Figure 7. SEM image of the sampled char gasified with steam (conversion=0.61) [29]

As described in the SEM results, gasification with iron is more likely to occur on the surface, as the added catalyst was attached to the surface of the char particle. Figure 8 shows the SEM image of an uncatalyzed char particle after 30 min of gasification at 800°C . . Though the scales in Figure 7 and Figure 8 are different, both of the images clearly reveal the surface performances of coal particles obtained under different

gasification conditions. The particle exterior in Figure 8 is rough due to the gasification reaction while no obvious pores are observed on the surface. The possible reason for the particle in the upper right hand corner of Figure 8 being eroded is that primary mineral exists appropriately in this part and so catalyzes coal gasification. In this situation, the SCM should be more suitable than the RPM. However, the SEM analysis is just an initial judgment in this work. The choice of model is mainly determined by analysis of the kinetic data.

Figure 8. SEM image of the char sample without iron after 30 min gasification at 800°C.

For further determining the merit of the two models, fitting results for the kinetic data collected at 900°C under catalytic and non-catalytic conditions are exhibited in Figure 9. The SCM performs better than the RPM in the data fitting. The RPM assumes that the reaction area enlarges as the internal surfaces of the pore structure increase during the gasification process, and then the area drops sharply due to the merging and the collapse of some pore structures in within the char. Thus, the RPM fitting in this work overestimates the gasification rate in the intermediate stage of the gasification, and underestimates the gasification rate in the later stage.

Figure 10 shows the gasification rates as a function of fractional carbon conversion with (a) 0 wt% Fe and (b) 3 wt% Fe during char gasification. There are some minor deviations from the SCM model prediction for the uncatalyzed coal at low conversions (<10 wt%) during gasification at lower temperatures (700 and 750°C). These are likely associated with start-up effects during the experiment and do not significantly affect the SCM accuracy, although they do contribute to the lower coefficient of determination (R^2) values for these two conditions shown in Table 2, which also lists the rate constant and shape factor obtained by nonlinear fitting for the SCM.

Figure 9. Fitting results for the kinetic data collected at 900°C under catalytic and non-catalytic conditions.

Figure 10. Gasification rates as a function of fractional carbon conversion with (a) 0 wt% Fe and (b) 3 wt% Fe.

The activation energies of char gasification were quantitatively evaluated by the Arrhenius expression:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where k is the reaction rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the ideal gas constant, and T is the reaction temperature. The kinetic constants A and E_a were obtained from the Arrhenius plot, as shown in Figure 11. The activation energy as obtained by the SCM was 92.7 kJ/mol for the untreated coal and only 58.3 kJ/mol with the addition of 3 wt% Fe. Kwon et al. studied the reaction kinetics of char-CO₂ gasification using four coals with different ranks based on the non-reactive core model, and found that the activation energies varied from 79.0 to 155.5 kJ/mol [30]. Thus, iron from a carbonate precursor significantly improves the kinetics of the Wyodak coal char gasification with CO₂.

Table 2. Kinetic Parameters Obtained by SCM for the Wyodak Coal Char Gasification.

Catalyst	T (°C)	$k_{SC}(*10^{-4} s^{-1})$	m	R ²
0 wt% Fe	700	0.4478	1.0308	0.9057
	750	0.8492	1.003	0.9700
	800	1.432	0.7558	0.9967
	850	2.391	0.6687	0.9985
	900	3.024	0.5803	0.9949
3 wt% Fe	700	1.196	0.5223	0.9975
	750	1.838	0.6220	0.9968
	800	2.544	0.5042	0.9872
	850	3.288	0.5078	0.9988
	900	4.122	0.4740	0.9911

Figure 11. Arrhenius plot for calculation of kinetic constants A and E_a .

3.3.3 Transformation of Iron Species and Proposed Catalytic Mechanism

The XRD results for the char samples with 3 wt% Fe after different gasification times are shown in Figure 12. The powder diffraction file (PDF) numbers and primary peak locations of the substances found in the samples are listed in Table 3. As shown in Figure 12(a), metallic iron is present at the beginning of the char gasification at 800°C. After 5 minutes of gasification, the peaks for metallic Fe are weakened, while FeO appears in the char sample. Metallic Fe and FeO are also observed in the XRD spectrum for the char sample after 30 minutes of gasification at 800°C.

The differences between Figures 12(b) and 12(c) are the FeO peaks become increasingly pronounced, while the peaks for metallic Fe become less prominent. With the consumption of carbon during char gasification, the CO concentration in the gas products declines and the gasification environment gradually shifts from a reducing atmosphere to an oxidizing atmosphere. Thus, more iron exists as FeO or other oxide forms. This is reinforced by the evidence that Fe_3O_4 is observed in the char sample after 120 min of gasification and the coal ash at the end of gasification at 800°C, as shown in Figures 12(d) and 12(e). FeO apparently is further oxidized in the CO_2 atmosphere to Fe_3O_4 , which remains stable at 800°C.

Figure 12. The XRD spectra of the char samples with 3 wt% Fe at 800 °C with different gasification time. ((a) 0 min; (b) 5 min; (c) 30 min; (d) 120 min; (e) the end of gasification)

Table 3. Primary Peaks and PDF Numbers of the Species Identified in the XRD Spectra.

Name	Main peaks (2θ)	PDF number
Ca ₂ Al ₂ SiO ₇	23.996°, 31.43°, 44.389°, 52.116°	89-6887
Fe	44.672°, 65.021°, 82.332°	99-0064
FeO	36.342°, 42.193°, 61.164°, 73.129°	46-1312
Fe ₃ O ₄	30.157°, 35.521°, 43.172°, 57.098°	88-0315
SiO ₂	20.756°, 26.638°, 36.541°, 39.466°	85-0798

Figure 13 shows The Mössbauer spectroscopy results related to the char samples with 3 wt% Fe after different gasification times, while the fitting parameters of the Mössbauer spectra are presented in Table 4. Char samples without added iron catalyst were also evaluated by Mössbauer spectroscopy, but there was not enough Fe present to obtain a spectrum. As shown in Figure 13(a), a peak comprising 34.1% of the spectral

area is observed with isomer shift and quadrupole splitting of 0.0 mm/s and 0.00 mm/s, respectively, indicating metallic Fe which appears to be the main iron species at the beginning of the gasification. Fe^{3+} in cementite is also present as 18.3% of the total iron. After 5 min of gasification, the cementite peak disappears, while metallic Fe and magnetite are observed and account for 24.0% and 11.9% of the total iron, respectively. 28.3% of the total iron exists in an unknown phase with non-specific parameters; however, it is proposed to be FeO, in accordance with the XRD results. After 30 min of gasification, magnetite disappears, and the spectral area for metallic Fe and the proposed FeO phase decline to 13.0% and increase to 66.8%, respectively. At the end of the gasification, magnetite is observed and comprises 91.8% of the total iron. These trends are generally consistent with the mineralogy observed from the XRD results.

It should be noted that even though only a few weight percentages of iron catalyst need to be added for iron based catalytic gasification process, the weight percentage of the spent iron catalyst in hydrocarbon-gasified ash can be raised to 15-20%, depending on the concentration of ash in raw or as-received coal. Thus, recycling the spent iron catalyst in the ash resulting from gasification process is beneficial not only to environment but also to the decrease in overall gasification cost, which can be realized using widely used magnetic Fe_3O_4 -containing material separation approach [31]. The iron oxide existed in the form of Fe_3O_4 instead of Fe_2O_3 in the ash, as shown in the XRD and Mossbauer spectroscopies of the result and discussion section of this research. The recycled iron catalyst can be mixed with coal proportionally and fed back to gasifier for reuses. This part of work will be report in a separated paper.

Table 4. Fitting parameters of the Mössbauer spectra.

sample	After pyrolysis	5 min gasification	30 min gasification	complete gasification
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velocity scale (mm/s)		+/- 10	+/- 10	+/- 10	+/- 10
spectrum temp (K)		295	295	295	295
ferric	IS	0.40	0.27	0.28	0.27
	QS	0.96	0.70	Q	0.79
	Width	0.27	0.60	0.70*	0.70*
	Area	4.2	33.1	20.2	8.2
FeO	IS		1.18	1.07	
	QS		-0.06	0.30	
	Width		0.68	0.52	
	Area		28.3	66.8	
cementite	IS	0.18			
	QS	0.01			
	Field	208.8			
	Width	0.31			
metallic iron	Area	18.3			
	IS	0.01	-0.01	-0.08	
	QS	0.00	0.01	0.08	
	Field	331.6	331.4	329.8	
magnetite	Width	0.28	0.31	0.57	
	Area	34.1	24.0	13.0	
	IS		0.55		0.66
	QS		0.07		0.01
magnetite	Field		463.9		462.4
	Width		0.68		0.34
	Area		8.2		60.0
	IS		0.18		0.27
magnetite	QS		0.03		-0.03
	Field		485.5		491.2
	Width		0.30*		0.25
	Area		3.7		31.8
χ^2		690.9	1123.5	2696.1	5329.9
χ^2_{norm}		1.3	2.2	5.2	10.3

IS = isomer shift in mm/s; QS = quadrupole splitting in mm/s; field magnetic field in Oe; Width = FWHM of peaks in mm/s; area is percentage of total spectral area.

* Parameter fixed.

Figure 13. Mössbauer spectra at 295 K of the 3 wt% Fe char samples under different conditions. ((a) 0 min; (b) 5 min; (c) 30 min; (d) the end of gasification)

The transformation of the iron species observed in this work can be explained by the phase equilibrium diagram for the Fe–O–C system and the CO concentration change in the gasification, as shown in Figure 14 [32] and Figure 15. Figure 15 shows the CO volume percentage in gas products as a function of reaction time in the catalytic gasification with CO₂ at 800 °C. The first data point in the figure was collected just before the introduction of CO₂. It can be seen that before gasification, the concentration of CO in the reactor is at a low level due to the low oxygen availability, which was

produced from the coal pyrolysis in nitrogen. Thus, when CO₂ was introduced into the reactor, the reaction of metallic Fe is able to take place as follows:

Subsequently, carbon participates in the reaction as follows:

These reactions lead to a sharp rise of the CO concentration in the reactor, and then the reaction of iron species mainly occurs with metallic Fe (R6) and FeO (R9), as indicated in Figure 14. Thus, no more magnetite is produced and finally it disappears in the char sample as Reaction 8 continues. This can explain the phenomenon that magnetite existed in the char sample after 5 min gasification, but was not observed after 30 min of gasification. The CO concentration in the gas products reaches a peak shortly after the beginning of the char gasification, and then declines gradually. When the CO concentration in the reaction system is maintained at a high level, the catalytic char gasification occurs mainly through the redox cycle, as Reactions 6 and 9 show. However, as the consumption of carbon and the CO concentration decrease, Reaction 6 increases while Reaction 9 is suppressed. FeO accumulates and metallic Fe is exhausted gradually under this condition. This proposed mechanism corresponds to the area change of metallic Fe and FeO in the Mössbauer spectra. As CO concentration decreases and FeO accumulates, magnetite generation restarts, as Reaction 7 shows. At the end of char gasification, the carbon is consumed and all FeO is oxidized to Fe₃O₄, in accordance with the XRD and Mössbauer spectroscopy results. Thus, the redox cycle in

the catalytic char gasification as Reaction 7 and Reaction 8 can be inferred when CO concentrations are low.

Figure 14. Phase equilibrium diagram for the Fe–O–C system with Boudouard equilibrium curve [32].

Figure 15. The volume percentage of CO in gas products as a function of reaction time in the catalytic gasification with CO₂ at 800 °C.

4. CONCLUSIONS

FeCO₃ was used as a catalyst precursor in Wyodak coal gasification with CO₂. During pyrolysis, the catalyst precursor was reduced to metallic Fe, while the tar

production rate decreased. This metallic Fe then underwent an oxidation process, $\text{metallic Fe} \rightarrow \text{FeO} \rightarrow \text{Fe}_3\text{O}_4$, in the CO_2 atmosphere during the coal gasification. The redox cycle between metallic Fe and FeO catalyzed the initial char gasification with CO_2 . The catalytic iron species changed to FeO and Fe_3O_4 in the later stage of the char gasification. SEM images visually support the catalytic effect of iron on char gasification, while the kinetic analysis by shrinking core model shows that the activation energy for the char gasification decreases from 92.7 kJ/mol (0 wt% Fe) to 58.3 kJ/mol (3 wt% Fe). FeCO_3 appears to be an effective catalyst for the Wyodak coal gasification with CO_2 .

ACKNOWLEDGEMENT

This work was supported by Wyoming Clean Coal Program, China Scholarship Council (201206430023), the US Department of Energy, and SIDCO Minerals Inc.

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Figure 1. Schematic diagram of catalytic coal gasification with CO₂ [(1a) N₂, (1b) CO₂, (1c) Ar; (2) mass flow controller; (3) heating tapes; (4) thermocouples and temperature scanner; (5) tube furnace; (6) ceramic wools; (7) coal sample; (8) temperature controller for heating tapes; (9) tar collector; (10) water-cooled condenser; (11) water-trap; (12) micro GC; and (13) data acquisition system].

Figure 2. Thermo gravimetric analysis (TGA) for raw Wyodak coal and the coal with iron [mass of coal: ~40 mg; TGA operation conditions [heating rate: 10 °C/min from 120°C to 900°C; carrier gas and its flow rate: N₂, 100 cm³/min].

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Figure 13. Mössbauer spectra at 295 K of the 3 wt% Fe char samples under different conditions. ((a) 0 min; (b) 5 min; (c) 30 min; (d) the end of gasification)

Figure 14. Phase equilibrium diagram for the Fe–O–C system with Boudouard equilibrium curve. [32]

Figure 15. The volume percentage of CO in gas products as a function of reaction time in the catalytic gasification with CO₂ at 800 °C.

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Table 1. Proximate and Ultimate Analyses of the Raw Wyodak Coal.

Table 2. Kinetic Parameters Obtained by SCM for the Wyodak Coal Char Gasification.

Table 3. Primary Peaks and PDF Numbers of the Species Identified in the XRD Spectra.

Table 4. Fitting parameters of the Mössbauer spectra.

Table 1.

Proximate Analysis	As Received (wt%)	Moisture Free (wt%)	DAF (wt%)
Moisture	17.81	-	-
Ash	7.17	8.72	-
Volatile matter	36.56	44.48	48.73
Fixed carbon	38.46	46.80	51.27
Total	100.00	100.00	100.00
Ultimate Analysis			
Moisture	17.81	-	-
Hydrogen ¹	2.80	3.40	3.72
Carbon	59.17	71.99	78.87
Nitrogen	0.76	0.93	1.01
Sulfur	0.35	0.43	0.47
Oxygen ¹	11.95	14.54	15.93
Ash	7.16	8.71	-
Total	100.00	100.00	100.00

¹Hydrogen and oxygen values reported do not include hydrogen and oxygen in the free moisture associated with the samples.

Table 2.

Catalyst	T (°C)	K _{SC} (*10 ⁻⁴ s ⁻¹)	m	R ²
0 wt% Fe	700	0.4478	1.0308	0.9057
	750	0.8492	1.003	0.9700
	800	1.432	0.7558	0.9967
	850	2.391	0.6687	0.9985
	900	3.024	0.5803	0.9949
3 wt% Fe	700	1.196	0.5223	0.9975
	750	1.838	0.6220	0.9968
	800	2.544	0.5042	0.9872
	850	3.288	0.5078	0.9988

	900	4.122	0.4740	0.9911
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Table 3.

Name	Main peaks (2 θ)	PDF number
Ca ₂ Al ₂ SiO ₇	23.996°, 31.43°, 44.389°, 52.116°	89-6887
Fe	44.672°, 65.021°, 82.332°	99-0064
FeO	36.342°, 42.193°, 61.164°, 73.129°	46-1312
Fe ₃ O ₄	30.157°, 35.521°, 43.172°, 57.098°	88-0315
SiO ₂	20.756°, 26.638°, 36.541°, 39.466°	85-0798

Table 4.

sample		After pyrolysis	5 min gasification	30 min gasification	complete gasification
velocity scale (mm/s)		+/- 10	+/- 10	+/- 10	+/- 10
spectrum temp (K)		295	295	295	295
ferric	IS	0.40	0.27	0.28	0.27
	QS	0.96	0.70	Q	0.79
	Width	0.27	0.60	0.70*	0.70*
	Area	4.2	33.1	20.2	8.2
FeO	IS		1.18	1.07	
	QS		-0.06	0.30	
	Width		0.68	0.52	
	Area		28.3	66.8	
cementite	IS	0.18			
	QS	0.01			
	Field	208.8			
	Width	0.31			
metallic iron	Area	18.3			
	IS	0.01	-0.01	-0.08	
	QS	0.00	0.01	0.08	
	Field	331.6	331.4	329.8	
magnetite	Width	0.28	0.31	0.57	
	Area	34.1	24.0	13.0	
	IS		0.55		0.66
	QS		0.07		0.01

magnetite	Field		463.9		462.4
	Width		0.68		0.34
	Area		8.2		60.0
	IS		0.18		0.27
	QS		0.03		-0.03
	Field		485.5		491.2
	Width		0.30*		0.25
	Area		3.7		31.8
	χ^2	690.9	1123.5	2696.1	5329.9
	χ^2_{norm}	1.3	2.2	5.2	10.3

IS = isomer shift in mm/s; QS = quadrupole splitting in mm/s; field magnetic field in Oe; Width = FWHM of peaks in mm/s; area is percentage of total spectral area. * Parameter fixed.

Graphical abstract

Graphical Abstract: SEM images of the char sample and the corresponding distribution of iron atom clusters from EDS.