

H₂ and CO_x Generation from Coal Gasification Catalyzed by a Cost-Effective Iron Catalyst

T. Popa^a, M. Fan^{a,*}, M. D. Argyle^b, M. D. Dyar^c, Y. Gao^a, J. Tang^d, E. A. Speicher^c, D. Kammen^e

^aDepartment of Chemical and Petroleum Engineering, University of Wyoming, Laramie, WY 82071

^bDepartment of Chemical Engineering, Brigham Young University, Provo, UT 84602

^cDepartment of Astronomy, Mount Holyoke College, South Hadley, MA 01075

^dDepartment of Physics and Astronomy, University of Wyoming, Laramie, WY 82071

^eEnergy and Resources Group, University of California, Berkeley, CA 94720

ABSTRACT

FeCO₃ was used for the first time to gasify a low-sulfur sub-bituminous Wyodak coal from the Powder River Basin (PRB) of Wyoming using a fixed-bed laboratory gasifier within steam environment at atmospheric pressure. The iron-based catalyst was active in both pyrolysis and gasification steps, but its oxidation state changed depending on the reaction conditions of gasification process. XRD and Mössbauer spectroscopy were used to establish the iron species and oxidation states of the catalyst during gasification. The active species of the catalyst, including magnetite (Fe₃O₄), wustite (FeO), and metallic iron, were determined by the steps of pyrolysis and gasification. The catalyst can significantly reduce the activation energy of the studied coal gasification process. It can considerably increase carbon conversion rate and H₂ production at 700°C.

Keywords: catalysis; coal gasification; ferrous carbonate; Powder River Basin coal; kinetics

1 INTRODUCTION

Integrated gasification combined cycle (IGCC) of coal offers the advantages of higher efficiency and capability of CO₂ and pollutant separation compared to conventional coal-fired power plants. One important step in IGCC is coal gasification, which occurs within an energy-intensive high temperature environment. Therefore, people are increasingly interested in using catalysts to improve coal gasification. Iron compounds are potential gasification catalysts due to their abundance, low cost, and environmentally friendliness. Several iron compounds have been tested to catalyze coal gasification and their effects on coal pyrolysis and char gasification as well as tar formation during the whole coal gasification process have been studied [1-5].

Ohtsuka et al. [1] used X-ray diffraction (XRD) to investigate the effect of three iron compounds on coal pyrolysis. When using FeCl₃ as the iron precursor, they reported the presences of both metallic α -Fe and FeO (wustite) when devolatilization was conducted in an inert atmosphere, and existence of Fe₃O₄ (magnetite) when devolatilization was performed within steam environment. The crystalline sizes of the three iron species were larger than 100 nm. The same research group also studied the effect of Fe₂(SO₄)₃. They obtained similar results, except for the appearances of FeS peaks within both inert and steam devolatilization environments. When Fe(NO₃)₃ was employed as the iron precursor in an inert atmosphere, α -Fe (<30 nm) and Fe₃C were detected, while a combination of small crystallites (<10 nm) of Fe₃O₄ with FeO were found when steam was used for devolatilization. In addition, the research group found that Fe(NO₃)₃, transformed

into fine particles of mixed iron oxides during devolatilization, was effective for steam gasification while chloride and the sulfate, converted to magnetite with a large crystallite size, were not effective. On the other hand, Song et al. [2] reported that $\text{Fe}(\text{NO}_3)_3$ was less active than FeSO_4 during pyrolysis of a sub-bituminous coal with the same iron loading (3 wt%) at 700-800°C. Yu et al. [3] loaded iron onto a brown coal using FeCl_3 solution and obtained metallic α and γ Fe in the pyrolysis step and magnetite during gasification. Domazetis et al. [4] reported that the char formed during pyrolysis of brown coal with added iron contained iron oxides and carbonates, as measured by X-ray photoelectron spectroscopy (XPS).

Coal tar is one of the byproducts formed during coal gasification. Tromp et al. [6], using gas-chromatography (GC) and gas-chromatography-mass spectrometry (GC-MS), identified that the volatile compounds from a pyrolysis process included varying amounts of polycyclic hydrocarbons. Zeng et al. [7] studied the tar and the soot generated by tar's secondary reactions, using Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy of the dissolved samples in tetrahydrofuran (THF), also found that the tar molecules were typically poly-aromatic hydrocarbons (PAH) substituted with functional groups or heteroatoms, such as alkyl chains, oxygen, nitrogen, etc.. Iron containing materials have also been tested for their effects on tar formation during coal gasification. Cypres et al. [8] found that iron oxides (Fe_2O_3 or Fe_3O_4) reduced both the primary devolatilization rate of coal (between 300 and 600°C) and the tar and gaseous hydrocarbon yields, while the composition of the investigated tar did not change. They also found that hematite iron had a greater influence than magnetite iron. Moreover, limonite ($\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$) of various origins [9], iron oxides (FeO , Fe_2O_4 , Fe_3O_4 , and Fe_2O_3) [10], ankerite ($\text{CaFe}(\text{CO}_3)_2$), sintered iron ore, and pelletized iron ore were evaluated by Nordgreen et al. [11] The concluded that metallic iron from pre-reduced

hematite (Fe_2O_3) was an effective catalyst and achieved almost 100% tar decomposition at 900°C.

Different mechanisms have been proposed by researchers to explain the effect of iron catalysts on the gasification of carbonaceous materials including coal. Based on their studies on the steam reforming of woody biomass in a fluidized bed at 500-700°C with an Fe/ γ -alumina catalyst, Matsuoka et al. [12] suggested that redox reactions take place on the iron oxide surface. Yu et al. [13] and Hermann and Huttinger [14] and Xu et al. [15] thought that the overall reactions with non-catalyzed steam carbon gasification occur on carbon particles and they are relatively simple, while those with iron-based steam gasification mainly proceed on the surface of iron species and much more complicated.

Obviously, the above-mentioned iron-based catalysts are beneficial to coal gasification. However, FeCO_3 has never been evaluated for its potential as a coal gasification catalyst. Compared to the other iron salts, FeCO_3 has its advantages. It is inexpensive and CO_3^{2-} is less harmful than SO_4^{2-} , NO_3^- , Cl^- to gasification equipment and environment. Thus, this research was designed to use FeCO_3 as a precursor for catalytic coal gasification and investigate the associated mechanism, carbon conversion kinetics, and yields of H_2 , CO and CO_2 .

2 EXPERIMENTs

2.1 Material preparation and characterization

2.1.1 Catalyst

The first step of FeCO_3 preparation was to make $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution by adding 50 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (99%, Alfa Products) to 125 ml distilled water, followed by titrating the solution

with excess 10 wt% Na_2CO_3 solution made with Na_2CO_3 (99.8 wt%, FMC Inc.), resulting in light green precipitate, FeCO_3 . The precipitate was filtered and washed with the sodium carbonate solution to remove SO_4^{2-} , then washed again with distilled water, dried at 92°C , and calcined in air at 250°C , at which the color changed to brown. The material was sieved, and the particles smaller than $125\ \mu\text{m}$ were retained and stored in an air-tight dark colored glass jar to prevent changes in the moisture content and structure of the prepared calcined FeCO_3 .

2.1.2 Gasified coal

Predetermined quantities of the iron catalyst were dry mixed with raw Wyodak coal from the Wyoming Powder River Basin (PRB). Then, distilled water was mixed with the resulting material using the incipient wetness impregnation method to produce the needed Fe-coal mixtures. 80 wt% of the coal particles used were smaller than $74\ \mu\text{m}$. The nominal loadings of iron on the coal were calculated on a dry and ash free (DAF) coal basis. A reference sample was prepared using only distilled water. The resulting Fe-coal mixtures were air-dried at 98°C (371 K) to constant mass and then stored in an air-tight receptacle to prevent further changes in moisture content or loss of volatile matter.

2.2 Characterization

Thermo-gravimetric analysis (TGA) tests were performed using a TA Instruments SDT Q600 apparatus. The first TGA operation step was to load $\sim 50\ \text{mg}$ coal sample into a ceramic capped alumina sample holder, which was followed by 10 minutes of isothermal equilibration, heating at $20^\circ\text{C}/\text{min}$ within $100\ \text{ml}/\text{min}$ flowing Ar or N_2 (Ultra High Purity (UHP), US Welding) environment to a maximum pyrolysis temperature of $1,200^\circ\text{C}$, and holding it at the

temperature for another 10 minutes for isothermal equilibration. The weight percentage of the char generated at a given temperature was calculated using the weight of the residual material (char) in the sample pan of the TGA apparatus at the particular temperature relative to the initial weight of coal sample.

The proximate analyses of the raw coal were performed according to ASTM D5142 and D5016. The ultimate analyses for raw coal and chars produced at 700, 800 and 900°C were accomplished using ASTM methods D5373, D5016, and D4239. The chemical composition of the coal ash was measured using ASTM D6349.

X-Ray Diffraction (XRD) analyses were performed on powdered coal samples in a Philips X'pert PW3040-MPD. Analyses were conducted using CuK α radiation with 2θ ranging from 15° to 85° with 0.010° steps and a time/step of 0.05 s. 0.05 to 0.10 g finely powdered samples were collected before pyrolysis, during pyrolysis at 420°C, after pyrolysis, and 10 minutes or 20 minutes after gasification with steam started.

Fourier transform infrared spectroscopy (FTIR)/Raman analyses were performed on a Nicolet Magna 760 FTIR spectrometer (Thermo Scientific). The instrument has a 1064 nm Nd:YVO₄ excitation laser, an XT-KBr beam splitter, a He-Ne laser for sample alignment, a InGaAs detector, and a computer for automated spectra collection and analysis.

Mössbauer spectra were acquired at 295 K, 80 K, and 4 K using a source of ~30 mCi ⁵⁷Co in Rh on a WEB Research Co. model WT302 spectrometer equipped with a Janus closed cycle He cooling system. For Mössbauer analysis, coal samples were mixed with sucrose under acetone and placed in a holder backed by Kapton® polyimide film tape. The pure coal sample was run without sucrose; others used ~40 mg of sample and ~260 mg of sucrose to dilute the sample and optimize spectral acquisition. Data were collected over a ± 10 mm/s velocity range in

2048 channels with acquisition times ranging from 12 hours to 6 days depending on the Fe content of the samples. Spectra were corrected for nonlinearity via interpolation to a linear velocity scale, which is defined by the spectrum of the 25 μm Fe foil used for calibration. All data were corrected to remove the fraction of the baseline due to the Compton scattering of 122 keV gamma rays by electrons inside the detector. All spectra were fit using Mexdisd [16].

2.3 Gasification

The catalytic gasification apparatus used in this research is shown in Figure 1. Gasification tests were conducted at a pressure slightly above the local atmospheric pressure ~ 75 kPa at the elevation of the gasification laboratory ($\sim 2,200$ m). Fe-coal samples were gasified in H_2O - N_2 mixtures.

About 5.0 g DAF coal was used for each gasification test. Initially, the coal sample was heated in N_2 with a flow rate of 4.1 ml/min at $20^\circ\text{C}/\text{min}$ to the desired gasification temperature, followed by introducing steam at a flow rate of 0.04 g/min. The gases used for conducting the catalytic gasification study are ultra-high-purity (UHP) N_2 (US Welding), O_2 (Air Liquide), CO (US Welding), and CO_2 (Praxair). The flow rates of the gases were controlled using mass flowmeters as shown 2) in Figure 1 (Porter Instruments series 201 with a 4 channel PCIM4 controller). Water addition was realized by a high pressure pump (3) (Scientific Systems-Lab Alliance Series 1) with a back pressure regulator (4) (GO Regulator). The liquid water was vaporized in a coil type vaporizer (5) surrounded with heating tape. The stainless steel tubing before and after the $\frac{1}{2}$ " (13 mm) diameter tubular stainless steel tube reactor (9) was heat traced (6), with the temperatures monitored by thermocouples (7), to preheat the gas/water vapor mixture and to prevent coal tar and water from condensation at the reactor outlet. Additional

insulation was installed as needed in different sections of the piping throughout the system. Ceramic wool (12) was inserted into the reactor to support the coal sample (11). The gasification temperatures (i.e., 700°C, 800°C, and 900°C) were adjusted in a tubular furnace (10, Thermolyne 21100). The tar and water in the product gas were separated from the syngas through a water-cooled condenser (15) and collected (22) for analysis. The pressure of the whole gasification system was regulated by another back pressure regulator (13, GO Regulator) and monitored using pressure gauges (16, 17). The reactor was protected against over-pressure by a pressure relief valve (8). Then the cleaned syngas passed through a desiccant-filled water trap (18) for further water removal prior to flow measurement (19). The syngas was then either vented to the fume hood or analyzed by a gas chromatograph (Agilent 3000A micro GC) (20) equipped with two micro-columns (18, 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 collected data were documented using a data acquisition system (21).

2.4 Coal tar and char sampling

The tar samples were collected together with the water from the reactor outlet stream by cooling the volatile matter produced during pyrolysis and gasification in a water/tar condenser (15), as shown in Figure1. The collections of tar and char were performed for both raw coal and 3 wt% Fe-coal samples at 700, 800, and 900°C under the conditions of only pyrolysis with a heating rate of 20°C/min in N₂ and pyrolysis followed by steam gasification with an H₂O flow rate of 0.04 g/min for 10 minutes and 20 minutes. After the chars were cooled in flowing N₂, the

samples were extracted and stored in N₂, while the tar samples were collected and stored in vials under N₂ to prevent property changes.

3. RESULTSS AND DISCUSSION

3.1 Characteristics of the Wyodak coal

As reported in Table 1, the moisture content of the PRB coal as received is nearly 21 wt%, which leads to the heating value of the coal as low as 21,527 kJ/kg (9,255 BTU/lb) while the heating value of the dry coal is 27,205 kJ/kg (11,696 BTU/lb). The volatile matter fraction is approximately 34.0 wt%. The sulfur content of the sub-bituminous PRB coal is about 0.4 wt%, lower than those produced elsewhere.. The oxygen content is a relatively high 16.0 wt%, which is favorable to reactivity improvement of the coal during its gasification. The analysis results of Wyodak coal ash are listed in Table 2. It should be mentioned that most of the cations in Table 2 [5] are inherent components of the accompanying minerals in coal, which during gasification will combine with the atoms adjacent to them in the minerals to form compounds, and therefore principally not playing a role in the catalytic cycle and merely forming coal ash and slag.

Gasification tests were started with a temperature ramp of 20°C/min to heat the coal to a predetermined temperature for pyrolysis followed by the introduction of steam. The analysis of the coal char produced at different temperatures are listed in Table 3 [5], which shows the elimination of H, O, S, and N from the structure of the material and correspondingly the increase in the concentration of C and ash in the resulting coal chars. Material balances of the gases produced during pyrolysis indicate that the materials are eliminated mostly as H₂, H₂O, CO, CO₂, N₂, various sulfur compounds, and coal tar.

3.2 Catalytic effect on coal pyrolysis

Raw coal and the 3 wt% Fe-coal sample were pyrolyzed using TGA and the results are presented in Figure 2. The weight percentage of the char generated at a given temperature was calculated using the weight of the residual material (char) in the sample pan of the TGA at the temperature relative to the initial weight of the coal sample. Figure 2 shows that during pyrolysis, the weight loss of the treated coal generally follows the same curve as the untreated coal does. The temperatures at which maximum rate of mass loss occurs, corresponding to light gas and coal tar releases as shown in the inset of Figure 2, is lowered from 443°C for the raw coal to 433°C for the 3 wt% Fe-coal. Another smaller maximum mass loss rate is centered at 719°C, which can be assigned to the reduction of iron oxides to elemental iron [11]. The differences between 3 wt% Fe-coal and raw coal become evident above 500°C, with slightly more mass loss for the treated coal above 750°C compared to the raw coal. These results indicate that iron is active not only during gasification but also during pyrolysis.

3.3 XRD

Figure 3 illustrates the XRD spectrum of the FeCO_3 calcined at 250°C. The strong characteristic peaks for hematite (Fe_2O_3) occur at 33.2°, 35.6°, 49.5°, 54.2°, 62.3°, and 64.2°, while the smaller peaks, e.g., at 31.2°, are those of siderite (FeCO_3) and the products of its decomposition during its thermal treatment [17], including wustite (FeO), e.g., at 42°, 61°, 36.2°, and magnetite (Fe_3O_4), e.g. at 62.6°. There may be some small quantities of sodium ferrite (NaFeO_2) with a small peak at 16.7°, but this determination is not definitive because the other stronger characteristic peaks associated with other minerals also appear in this region.

The upper spectrum in Figure 4 is the XRD of the raw coal mixed with the iron catalyst, while the lower one in Figure 4 is the XRD for the catalyst, which is duplicated from Figure 3 for convenient comparison, to highlight the peaks characteristic to the catalyst relative to the peaks specific to the coal's organic material and its accompanying minerals. In addition to the peaks identified in Figure 3, the wide peaks at $\sim 21.5^\circ$, 26.5° , and $\sim 45.5^\circ$ are characteristic ones of carbon compounds [15] (e.g., graphite) in coal, while other large peaks are assigned to clay compounds and various carbonates [2].

Figure 5 contains the XRD data for the material obtained from pyrolysis in a N_2 atmosphere by ramping temperature from ambient ($\sim 25^\circ\text{C}$) to 420°C at the rate of $20^\circ\text{C}/\text{min}$. The presence of strong peaks for magnetite (Fe_3O_4) at 35.5° and 62.6° reveals that the initial iron compounds were transformed into magnetite in the reaction environment. This evidence is reinforced by the disappearance of the twin peaks of hematite (Fe_2O_3) at 62.3° and 64.2° . The wide peaks at 26.5° and 45.5° become sharper, showing the onset of graphitization of the pyrolyzed coal. Also visible are other large peaks, assigned to clay compounds and several carbonates [2].

Figure 6 contains the XRD data for the material obtained after a high temperature pyrolysis during which the temperature was increased from ambient to 800°C at the rate of $20^\circ\text{C}/\text{min}$ in a N_2 atmosphere. Compared to those in Figures 4 and 5, the peaks at 26.5° and 45.5° are more pronounced, demonstrating that the graphitization degree of the pyrolyzed coal has increased. This spectrum reveals the formation of cementite (Fe_3C), characterized by a group of peaks centered at 45° and a more pronounced peak at 83.1° , which are mixed with the characteristic peaks of carbon and metallic Fe, with peaks at 43.9° , 51.2° , and 75.3° .

Figures 7 and 8 are the XRD spectra for the materials collected following pyrolysis at 800°C plus 10 and 20 minutes, respectively, of gasification with steam. After only 10 minutes of steam introduction, the intensity of the peaks characteristic of FeO (wustite) increases, along with the peaks of metallic iron, while the peaks characteristic of Fe₃C begin to decrease in intensity, which indicates that a part of Fe₃C was transformed to iron and probably some of the finely dispersed metallic iron was reoxidized to iron oxides. The trend becomes clear in Figure 8 with the sample obtained after 20 minutes of gasification. The cementite peaks almost disappear (e.g., 83.1°), while metallic iron peaks remain (e.g., 75.3° and 82.6°) and peaks assigned to iron oxides, specifically wustite (61°, 72.9°, and 76.6°), are present.

3.4 Mössbauer spectroscopy

Figure 9 shows the Mössbauer spectra for the catalyst and coal samples. The detailed data and parameters are given in Table 4. There was no Fe in the raw coal and thus no Mössbauer spectrum after a 6-day run. Figure 9a, which contains the spectrum of the raw coal and catalyst prior to pyrolysis, shows that of all the iron in the catalyst is Fe³⁺ in the form of hematite (Fe₂O₃). No other Fe-bearing phases are observed.

The Mössbauer spectra of the after-pyrolysis material collected are significantly more complex presented in Figures 9b and 9c. The spectra of the prior-to-gasification material in Figure 9b show a large doublet (43% of the total area at 295K) that is assigned to higher oxidation state iron, e.g., FeO₄ groups [18], with a strong signature of metallic Fe accounting for ~32% of the total Fe and smaller peaks that likely represent Fe₃C [19]. A small doublet representing 7% of the total Fe has parameters consistent with six-coordinated Fe³⁺, but is too small to be identified.

After 10 minutes of gasification (Figure 9c), some of the higher oxidation state iron accounting for 28% of total iron is reduced to a ferric nanophase oxides representing 24% of the total Fe. Sextets assigned to FeOOH and metallic iron, accounting for 9% and 40% of total iron, respectively, are observed. There is no evidence for cementite in the spectra of the gasified samples. These trends are generally consistent with the mineralogy observed with XRD.

3.5 FTIR of the coal tar

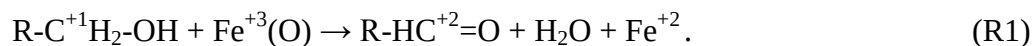
Figure 10 shows the FTIR analysis of the coal tar condensed in the collection system by the water-cooling unit (15) in Figure 1. The large peak at $\sim 3450\text{ cm}^{-1}$ (characteristic of water) has two shoulders, one at $\sim 3150\text{ cm}^{-1}$ characteristic to H present in substituted aromatic rings and a smaller one at $\sim 2950\text{ cm}^{-1}$ characteristic of H in CH_2 structures (aliphatic hydrocarbons or branches). The ratio of these two peaks is $H_{\text{aro}}/H_{\text{ali}} > 1$, which highlights the aromatic character of the coal tar collected. This conclusion is reinforced by the presence of the two peaks at ~ 1630 and 1550 cm^{-1} ($\text{C}=\text{C}$ aromatic ring stretching vibrations), shifted due to various degrees of ring substitution, while the aromatic H out of plane bend at low degrees of substitution and also aromatic ring torsions display a wide band with many overlaps over $500\text{-}900\text{ cm}^{-1}$. The presence of aliphatic groups is indicated by the small peak characteristic for C-C-C bending at $\sim 1010\text{ cm}^{-1}$, the peak at $\sim 2950\text{ cm}^{-1}$ (H in aliphatic CH_2 structures mentioned previously), and by the peak at 1400 cm^{-1} characteristic of H in aliphatic CH_3 structures [20] and also for CH_2 and CH_3 deformations and C-O-H in-plane bending. All four spectra are similar. However, there are some important differences for the bottom two spectra in Figure 10, which are of the tar collected from the 3 wt% Fe catalyzed coal samples. Compared to the spectra for the samples without the catalyst, several peaks are absent, including the small peaks at 1250 cm^{-1} (assigned to C-O bond

stretching), the peak at 1100 cm^{-1} (assigned to organic O-H stretching), and the double peaks at 2366 and 2328 cm^{-1} , which could be the products of various physical phenomena (e.g., overtones), but can be assigned to the CO_2 asymmetric stretch. The 1630 and 1550 cm^{-1} peaks for the coal tar produced from pyrolysis only (without gasification) in the presence of the iron catalyst have a peak height ratio larger than one (i.e., the 1630 cm^{-1} peak is larger), while all the other samples displayed a ratio smaller than one (i.e., the 1550 cm^{-1} peak is larger). The implication of this declining ratio is discussed in the following section. The peak of C=O stretching (from ketones, aldehydes or carboxylic acids), expected in the interval $1690\text{-}1780\text{ cm}^{-1}$ [20] is absent, although it might be shifted.

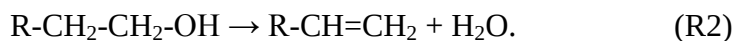
3.6 Pyrolysis

The iron catalyst at the beginning of the pyrolysis process, as shown by the XRD (Figure 3) and Mössbauer spectroscopy [Figure 9(a)] is comprised mostly of hematite (Fe_2O_3), siderite (FeCO_3), various oxides, and possibly ferrites. After mixing with coal and drying, the catalyst particles are in close contact with coal particles. When coal was heated in the absence of oxygen, the pyrolysis process produces variable quantities of H_2 , CH_4 , CO , and CO_2 , together with complex mixtures of organic substances (coal tar), in the vapor phase in the presence of the solid coal residue (char). Thus, the reaction environment is reducing in nature, which causes the decomposition of the traces of iron carbonate to iron oxides [11] and the reduction of iron oxides to iron and iron carbide above 719°C , as shown by the TGA, XRD, and Mössbauer analyses. This reduction was previously discussed with the TGA data, in which the decrease in the maximum mass loss rate by 10°C from 443°C for the raw coal to 433°C for the catalyzed coal can be explained by the transformation of various iron oxides to magnetite, as evidenced by the

XRD analysis (Figure 5). The cut temperature for the reactor outlet gases collected as liquid coal tar was set by the water-cooled condenser shown as item 15 in Figure 1) at $\sim 25^{\circ}\text{C}$. The addition of the iron catalyst to the coal caused the dynamic pressure drop in the tubing to decrease due to less tar condensation and also resulted in a smaller quantity of tar collected at the end of the test, which suggests that the tar was more volatile. TGA analysis shows a relatively small influence of the catalyst during pyrolysis, and indeed FTIR analysis shows very similar spectra of high aromatic character, as previously described in last section. However, the addition of the iron catalyst produced tar without IR peaks at 1250 cm^{-1} resulting from C-O bonds stretching and 1100 cm^{-1} due to the stretching of organic O-H. The absence of those peaks suggests dehydroxylation of the molecules present in the coal tar under the influence of iron catalyst. This reaction could be realized through at least two mechanisms. The first one is based on redox mechanism, where the carbon bearing the -OH bond is oxidized on the iron catalyst and transformed to aldehydes/ketones. A possible reaction that generates aldehydes is



The reaction, resulting from the redox ability of magnetite [21], is predicted by various oxygen transfer models on iron catalysts during interaction with coal at high temperature [4, 14, 22]. Therefore, in the collected coal tar, it was expected to find a peak generated by C=O stretching (from ketones, aldehydes, or carboxylic acids) in the interval $1690\text{-}1780\text{ cm}^{-1}$ [20]. However, unless the peak is radically shifted to $\sim 1630\text{ cm}^{-1}$, which is unlikely, the expected peak was not detected. The second mechanism is the dehydration of the coal tar with concomitant production of double bonds (alkenes) or



The reaction (R2) is generic. The -OH groups can be present on secondary or tertiary carbon also. In this case, the reaction would produce a number of C=C structures, detectable by their characteristic peaks, but would also increase volatility of the coal tar by decreasing the number of hydrogen bonds present. The peak at 1630 cm^{-1} is typically assigned to C=C stretching either in ring (aromatic) structures or in alkenes (aliphatic) structures. For the case of the coal tar collected after the pyrolysis in the presence of the iron catalyst, this peak is larger than the peak at $\sim 1550\text{ cm}^{-1}$ due to the C=C ring stretch, while in the sample collected after another 10 minutes of gasification, it becomes smaller, suggesting the evaporation of the substances generating a larger peak at 1630 cm^{-1} . The observation indicates a water gas shift (WGS) reaction associated mechanism, which is a mediated oxygen transfer from water to CO via adsorbed OH groups, catalyzed by magnetite [21], where CO and H_2 are present, together with CO_2 . This type of dehydration forming C=C bonds in organic molecules is surprising for magnetite and is more common for acidic catalysts, but also occurs on magnesium substituted alumina (Mg_yAlO_x) [23] and alumina phosphates loaded with transition metals [24].

3.7 Gasification

Catalytic effect of FeCO_3 on gasification kinetics

The kinetics of coal gasification was evaluated in temperature range of 700-900°C with the shrinking core model [5]:

$$\frac{dX}{dt} = k_{sc}(1-X)^{2/3} \quad (\text{E1})$$

where X represents carbon conversion fraction, t is time, and k_{sc} is the specific carbon conversion rate constant. Figure 11 is the Arrhenius plot showing the effect of temperature on the

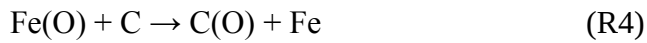
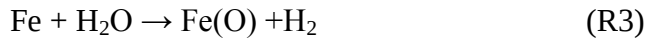
gasification reaction rate constant, k_{SC} obtained with shrinking core model for both the raw coal and the 3 wt% Fe coal. Using the shrinking model, the apparent activation energy results were 89.5 kJ/mol for the untreated coal, which decreased to 50.6 kJ/mol for the coal containing 3 wt% Fe. For comparison, another value reported in the literature for similar raw coal based on the random pore model is 102.3 kJ/mol [5]. Figure 12 contains a point around 770°C which corresponds to approximately equal values of the reaction rate constant for the catalyzed and uncatalyzed systems.

Catalytic gasification mechanism

Figure 12 compares the H_2 , CO, and CO_2 generated normalized per carbon in the char for coal samples untreated (dashed lines) and with 3 wt% Fe addition (solid lines) at 700°C and 900°C during the first 200 minutes of the experiments. As the reactor reaches the reaction temperature, there is an induction period of from 10 to 25 minutes before the catalytic reactions begin, which can be linked with phase transformation in catalytic material shown by XRD and Mössbauer analyses discussed earlier. The time required for the phase transformation is decreased as the temperature increases. After this induction period, the catalytic reaction becomes evident. The effect of the iron catalyst on H_2 productions at both 700°C and 900°C (Figure 12a) are obvious. In the 200-minute gasification period, 0.95 and 1.20 moles of H_2 were generated at 700°C with 1 mole uncatalyzed and catalyzed carbons in char, respectively. At 900°C, the difference becomes more produced since the quantity of H_2 generated with catalyzed char is about 300% higher than that with uncatalyzed char. The quantities of CO generated at 700°C with catalyzed and uncatalyzed chars within the same gasification period are almost same

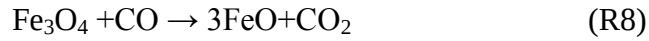
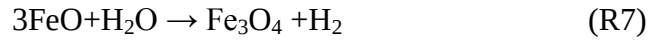
while about 12% more CO was produced with catalyzed char than uncatalyzed char at 900°C, as demonstrated in Figure 12b. The amounts of CO₂ (Figure 12c) resulting from 200 min gasification of catalyzed coal chars at 700°C and 900°C are 13% and 25% higher, correspondingly.

The accepted reaction model [13, 14] states that metallic iron, after reacting with steam, generates hydrogen and a layer of iron oxide on the surface of the particle (R3); this oxide layer reacts with nearby carbon which can reduce iron oxide to metallic iron and generate carbon monoxide (R4), followed by the desorption of the carbon monoxide, as summarized in the following reactions [13, 14]:



The model presumes the iron species present in catalyst is Fe⁰ and that the reaction takes place only if carbon is present in proximity of the metallic iron particle. The quantity of H₂ generated during the catalytic cycle is equal to the quantity of H₂ generated in an uncatalyzed cycle, as shown in the overall reaction (R6). Also, because of the low mobility of iron, the rate of reaction will decrease if the interface between the catalytic particle and coal particles becomes drained of carbon. This theoretical model with short distance interaction is consistent with the experimental observations and can mathematically be explained using shrinking core reaction model [25], which presumes that as the reaction progresses, the reactants and products have to pass through a layer of ash, with the reaction taking place at the shrinking core surface of unreacted material.

Another way that H₂ can be generated is by the WGS reaction (R10) on FeO (wustite) with surface defects, with the CO₂ produced being consumed by the Boudouard reaction (R9). The net result of these reactions remains the overall gasification reaction (R6):



The sum of R7 and R8 is the water-gas-shift (WGS) reaction (R10):



In this case, the reaction will not require the presence of carbon in the immediate vicinity of the catalyst because the CO₂ formed can easily transport through the gas phase to react at longer distances with the carbon in coal. The consequence of this reaction model is that the quantities of CO₂ and H₂ produced with iron catalyzed coal is larger compared with the uncatalyzed coal due to the water-gas-shift reaction. The uncatalyzed and slow Boudouard reaction determines the overall reaction rate (and thus the CO quantity will be similar or lower to that of uncatalyzed gasification), while the catalyzed and faster WGS reaction will produce more H₂ and CO₂.

Table 5 and figures 13 and 14 compares the quantities normalized per char carbon of CH₄, CO and CO₂, and H₂ generated by reaction with H₂O during gasification of coal at 700-900°C for the uncatalyzed reaction and iron catalyzed samples. Comparing the quantities of CO and CO₂ produced during gasification in the catalyzed and uncatalyzed case, the quantities produced appear to be the result of the opposing trends with temperature for the equilibrium

constants for the WGS and Boudouard reactions. The equilibrium constant for the exothermic WGS reaction decreases with increasing temperature, as while the equilibrium constant for the endothermic Boudouard reaction increases.

The comparison between the quantities of CO and CO₂ generated, normalized for the quantities of carbon present in the char at the end of pyrolysis as function of temperature (Figure 13 and table 5), shows that the presence of the iron catalyst generates slightly higher CO₂ and less CO compared with the uncatalyzed case which points toward the activity of iron oxides in the WGS reaction.

The quantities of H₂ normalized on the carbon present in char generated by reaction with H₂O during gasification for the iron catalyzed reaction are larger (Table 5 and figure 14) at lower temperatures and become similar at higher temperature compared to the uncatalyzed reaction. The increased H₂ quantity at lower temperature is a result of the water-gas-shift reaction (R10), which suggests a FeO-Fe₃O₄ [26] couple was present within the reaction environment in smaller quantities as the temperature of the tests was increased. The values H₂ generated by reaction with H₂O normalized on the carbon present in char were calculated by subtracting from the values of H₂ produced during gasification the quantities of hydrogen left in the char structure after pyrolysis (Table 3) and normalizing the result on the carbon present in char. As shown in Figure 14 in the case of the iron catalyst, there are larger quantities of H₂ generated per carbon from char for temperatures below 850°C, pointing again to the presence of iron oxides in the catalytic mass, while above 850°C, the quantity becomes almost the same, which suggest a catalytic mechanism driven by metallic iron.

The FTIR and XRD analyses of the tar mentioned in the earlier section suggests the participation of magnetite (Fe₃O₄) in coal pyrolysis. The data in Figures 7-9 show that metallic

iron, iron carbide, and $\text{FeO-Fe}_3\text{O}_4$ are present during gasification, which are catalysts for hydrogen generation. Thus, the wustite-magnetite couple appears also to be the active species during gasification step, but metallic iron was present during the fast gasification period. For the pyrolysis step, it is debatable which phase of iron was active for the production of the more volatile tar components, but the phase equilibrium diagram for the temperatures used [25, 26] as seen in Figure 15) indicates the stability of magnetite during the temperature interval of the maximum pyrolysis rate, confirmed by XRD presented in Figure 5.

The reduction process for iron oxide has been used since ancient times in iron metallurgy. This process occurs as function of the temperature and concentration of CO, while the CO concentration in systems containing char is governed by the Boudouard reaction (R9). According to the phase equilibrium diagram for the Fe-O-C system with the Boudouard equilibrium curve plotted in Figure 15, the reduction of iron oxides follows the concentration of CO at different temperatures. For example, at 433°C, the maximum temperature for the devolatilization rate during coal pyrolysis based on the TGA analysis, the Fe-O-C equilibrium diagram shows that the stable iron phase is magnetite (Fe_3O_4), which is in accordance with the XRD results for the material collected after pyrolysis at 420°C, and suggests that the dehydration reactions observed using FTIR can be attributed to magnetite.

According to the curve for the Boudouard reaction given in Figure 15 [27], within higher than 700°C temperature range, metallic iron becomes the stable phase. Our TPR measurements show the peak attributed to this process at 719°C. From this point on to higher temperatures, various phases of reduced iron are stable and their phases are influenced by the interactions with other components [28] and the oxidizing or reducing environment, indicated by the concentrations of steam, H_2 , etc. [25, 26]. The XRD and Mössbauer data show that at 800°C,

after the pyrolysis step, the iron phases present are metallic iron and cementite (Fe_3C). After gasification was initiated by the introduction of steam, the cementite phase started to disappear while the metallic iron phase signal became larger, with some weak peaks attributed to iron oxides (wustite). The same analysis for different temperatures explains the increase in H_2 production due to more oxides, probably magnetite, as superficial oxide is formed on wustite, as shown in R7 and R8, and the decreased reaction rate constant at higher temperature, due to the increased formation of iron carbide (Fe_3C) which seems to be inert for gasification and WGS reactions. After the steam is introduced, cementite transforms in iron, but as the reaction progresses, in the vicinity of the newly formed iron, ash also appears to be formed; thus, reaction R4 does not have the required carbon to proceed. This phenomenon was addressed by using a composite catalyst, which will be reported in a separate paper.

4 CONCLUSIONS

The addition of iron carbonate as a catalyst is beneficial to gasification of coal in terms of increased coal conversion rate and tar mitigation as well as H_2 productions at low temperatures. The iron catalyst used in this research can greatly reduce the activation energy of the gasification of the PRB coal while its effects change with gasification process and condition. There is an induction period before the catalyst becomes active, apparently due to phase transformations under reaction conditions, which is supported by comparing the amount of the gases generated per carbon in char with untreated coal and that with the addition of iron and the data of XRD and Mössbauer analyses. Various iron species catalyze the different steps of the whole coal gasification process.

ACKNOWLEDGEMENTS

The research was founded by SIDCO Minerals Inc. and the Wyoming Clean Coal Program, and US Department of Energy. The authors sincerely thank Mr. Bill Fuerst for his great support and help.

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List of Figures

Figure 1. Schematic diagram of catalytic coal gasification [(1a) N₂, (1b) O₂, (1c) CO, (1d) CO₂; (2) mass flow controller; (3) high pressure pump; (4) back pressure regulator; (5) boiler; (6) heat traced stainless steel tubing; (7) thermocouples; (8) pressure relief valve; (9) stainless steel reactor; (10) furnace; (11) coal; (12) ceramic wool stopper; (13) back pressure regulator; (14) three way valve; (15) water-cooled condenser; (16) and (17) pressure gauges; (18) water-trap; (19) flow meter; (20) gas chromatograph (GC); and (21) data acquisition system, (22) water condensing and tar collection].

Figure 2. Thermogravimetric analysis (TGA) for coal samples untreated and treated with FeCO₃ addition (3 wt% Fe) [mass of coal: ~50 mg; TGA operation conditions (heating rate: 20°C/min; carrier gas-Ar flow rate: 100 ml/min; maximum pyrolysis temperature: 1,200°C].

Figure 3. XRD of the iron catalyst

Figure 4. XRD of the iron catalyst mixed with raw coal

Figure 5. XRD of the iron catalyst and coal after pyrolysis at 420°C [mass of DAF coal: 5 g; N₂ flow rate: 4.1 ml/min]

Figure 6. XRD of the iron catalyst and coal after pyrolysis at 800°C [mass of DAF coal: 5 g; N₂ flow rate: 4.1 ml/min]

Figure 7. XRD of the 3 wt% Fe coal after pyrolysis (T_{max}: 800°C) and 10 minutes of gasification [mass of DAF coal: 5 g; H₂O: 0.04 g/min; N₂ flow rate: 4.1 ml/min; T: 800°C].

Figure 8. XRD of the 3% Fe coal after pyrolysis (T_{max}: 800°C) and 20 minutes of gasification [mass of DAF coal: 5 g; H₂O: 0.04 g/min; N₂ flow rate: 4.1 ml/min; T: 800°C].

Figure 9. Mössbauer spectra at 295 K of the iron catalyst and coal
[a): before pyrolysis (mass of DAF coal: 5 g; N₂ flow rate: 4.1 ml/min);
b): after pyrolysis (mass of DAF coal: 5 g; N₂ flow rate: 4.1 ml/min; T: 800°C);
c): after pyrolysis and 10 minutes of gasification (mass of DAF coal: 5 g; N₂ flow rate: 4.1 ml/min; H₂O flow rate during gasification: 0.04 g/min; T: 800°C)]

Figure 10. FTIR analysis of the coal tar collected during pyrolysis (max. T: 800°C) and 10 min gasification [mass of DAF coal: 5 g; H₂O: 0.04 g/min; N₂ flow rate: 4.1 ml/min; T: 800°C] for the untreated and treated with 3 wt% Fe coal samples

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Figure 14. Comparison between moles of H_2 produced from steam for one mole of char C during coal gasification for samples untreated and treated with $FeCO_3$ (3 wt% Fe) [mass of DAF coal: 5 g; H_2O : 0.04 g/min; N_2 flow rate: 4.1 ml/min; gasification temperature: 700 - 900°C]

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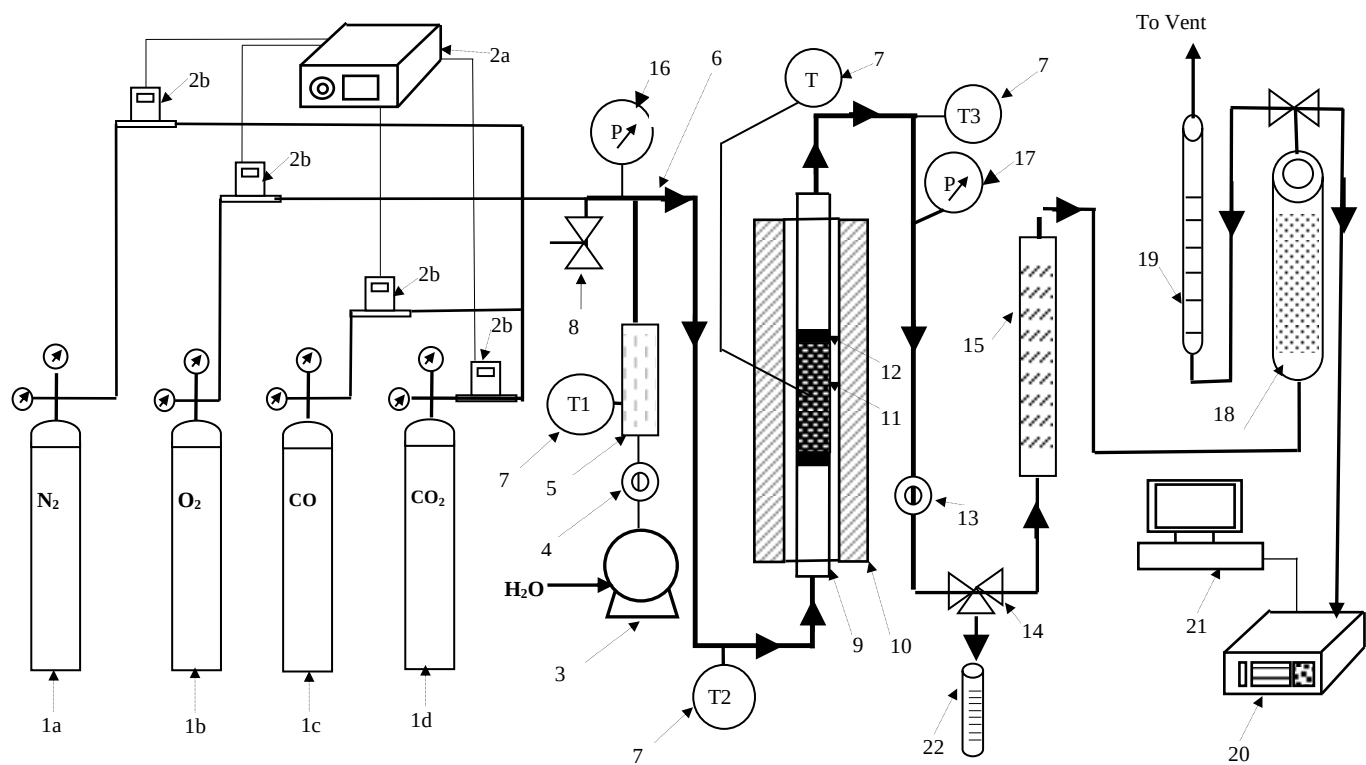


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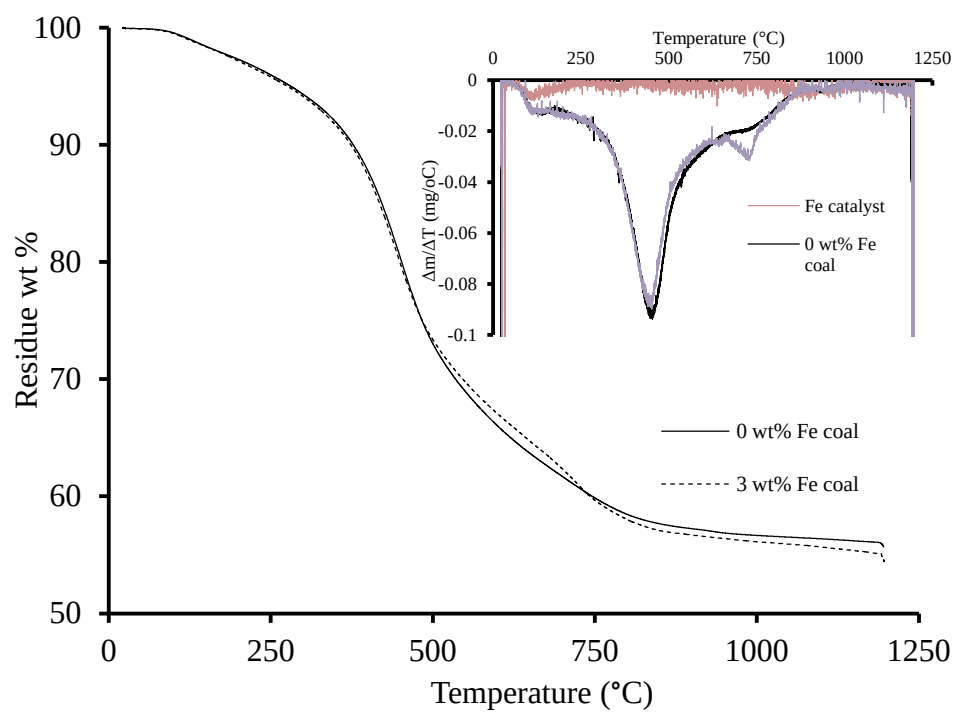


Figure 2

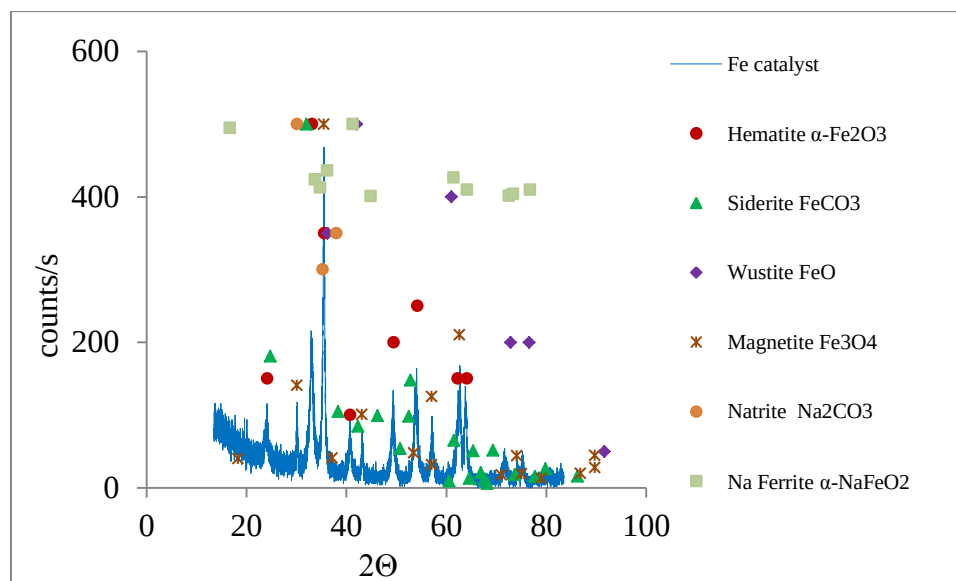


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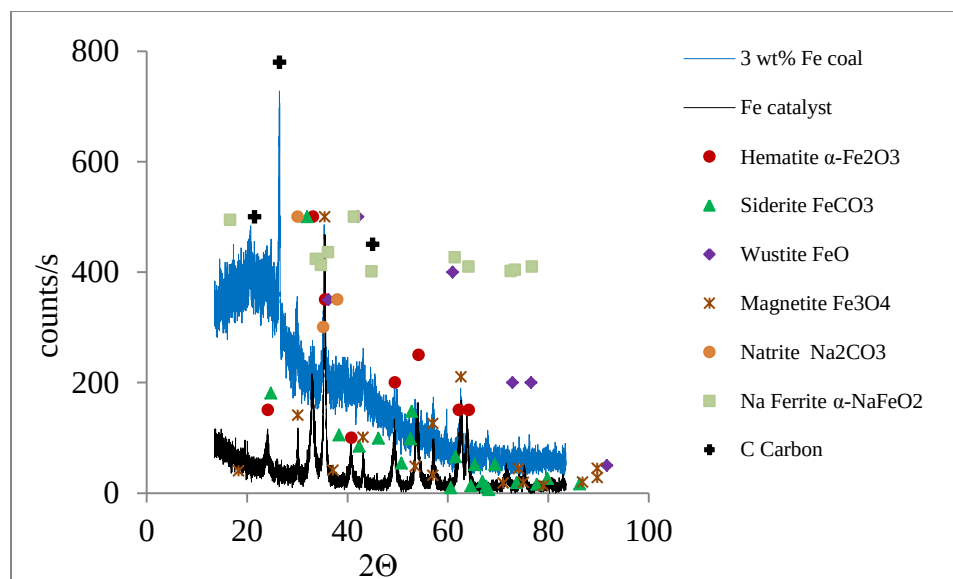


Figure 4

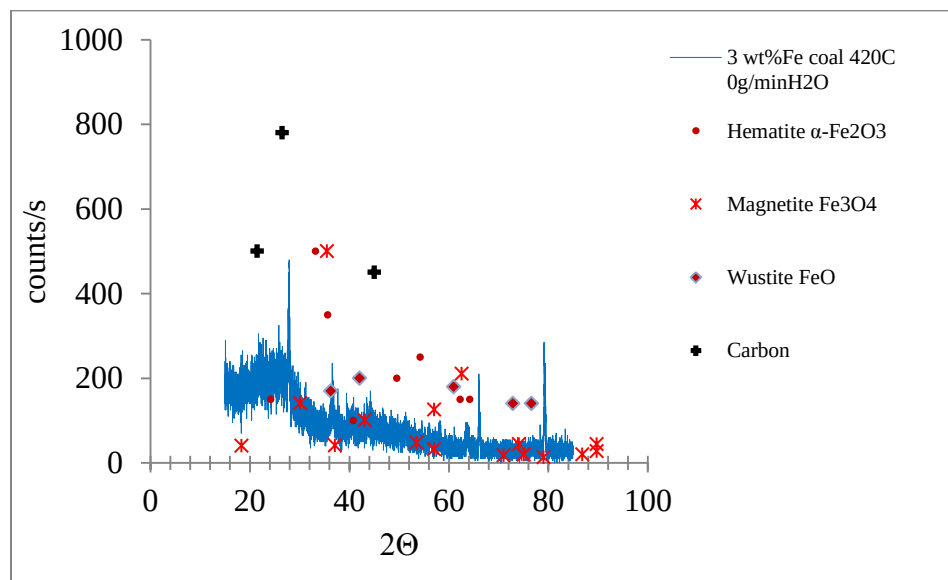


Figure 5

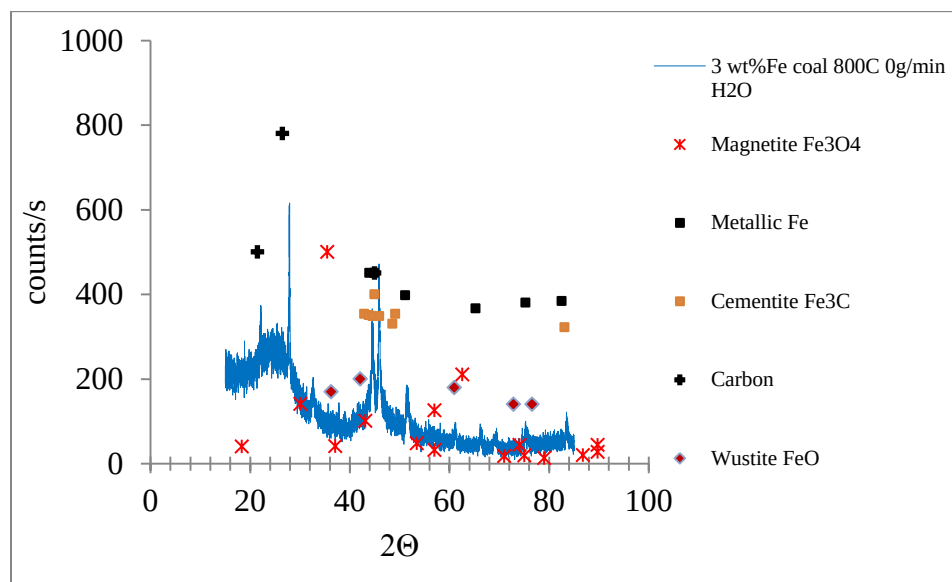


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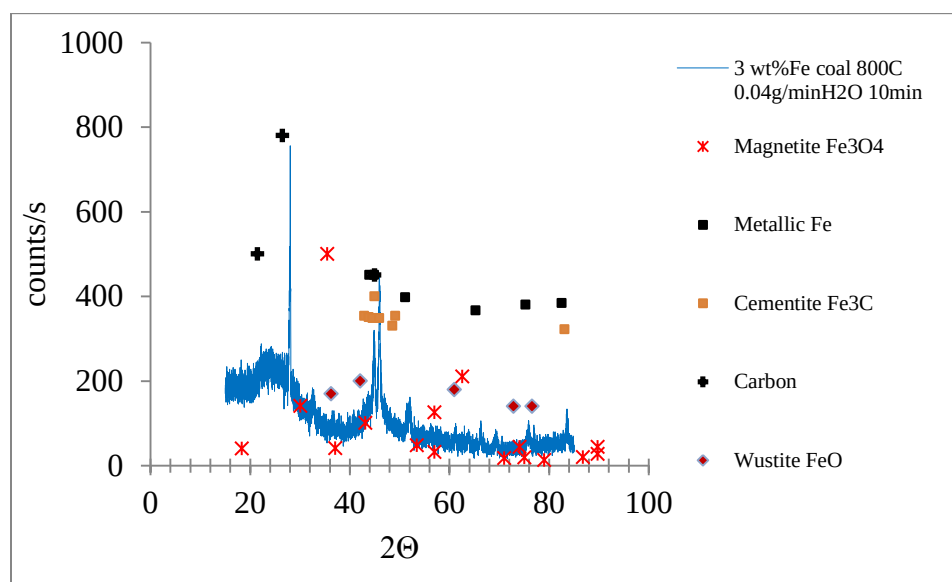


Figure 7

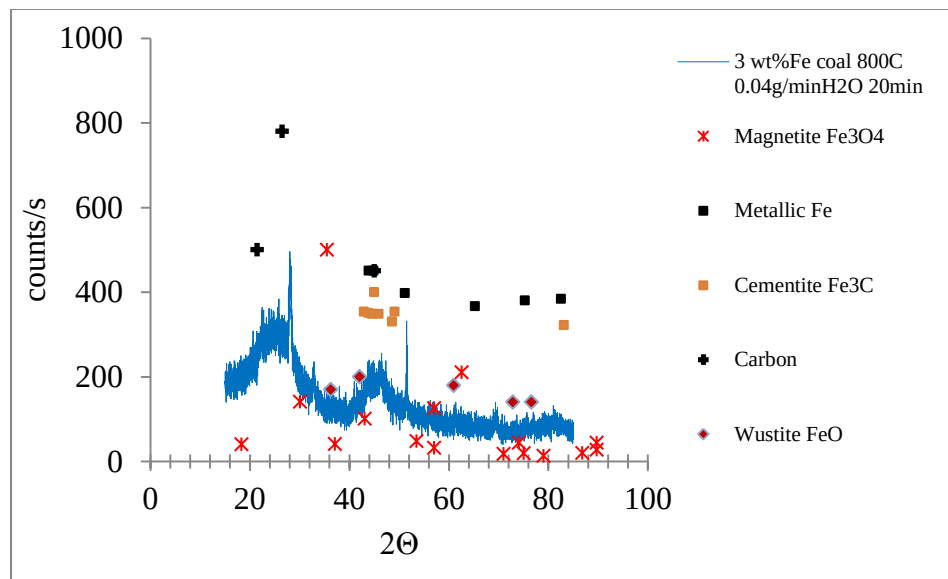


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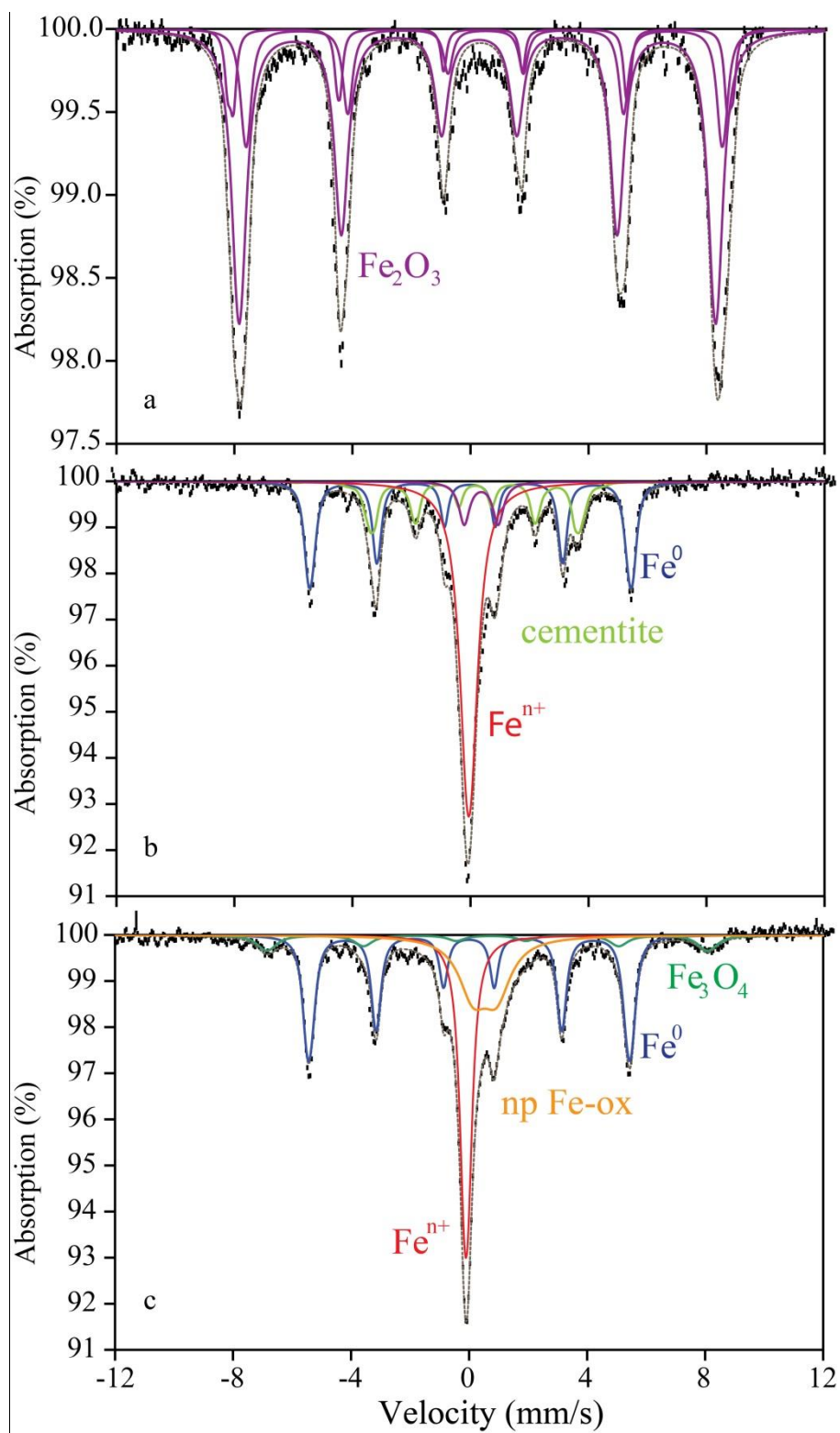


Figure 9

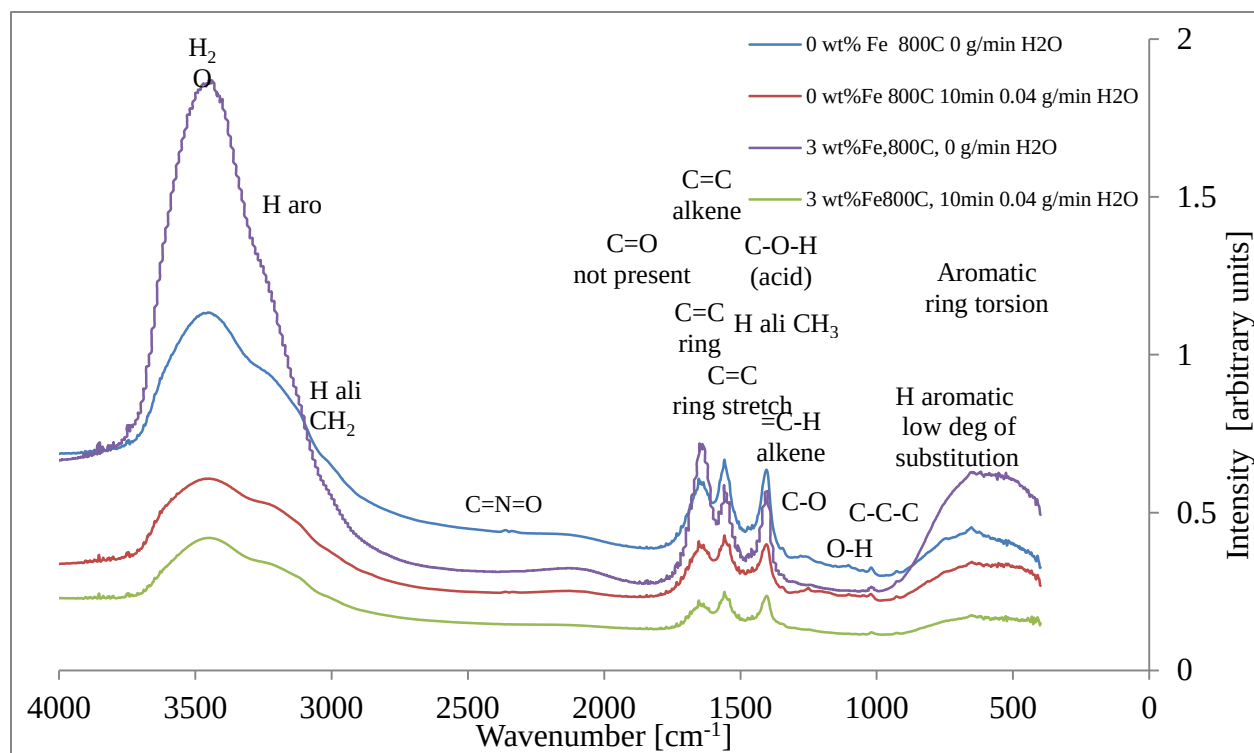


Figure 10

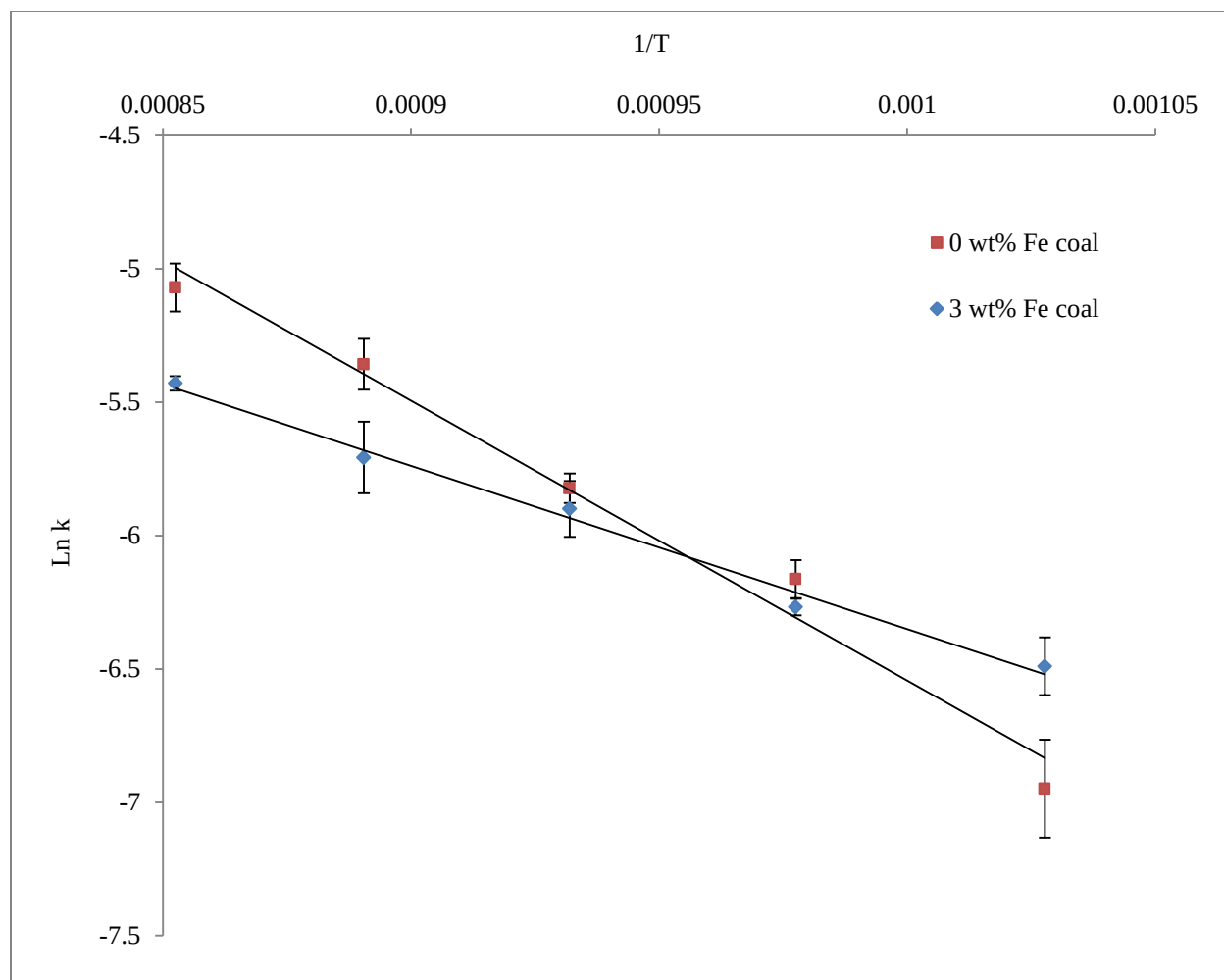
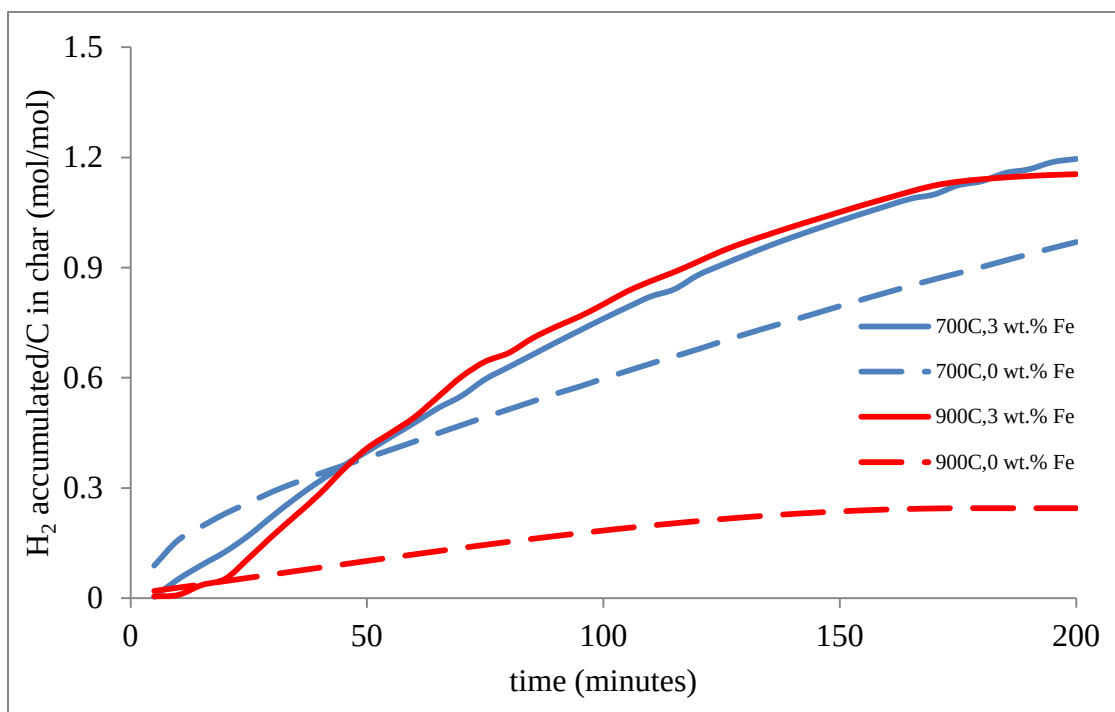
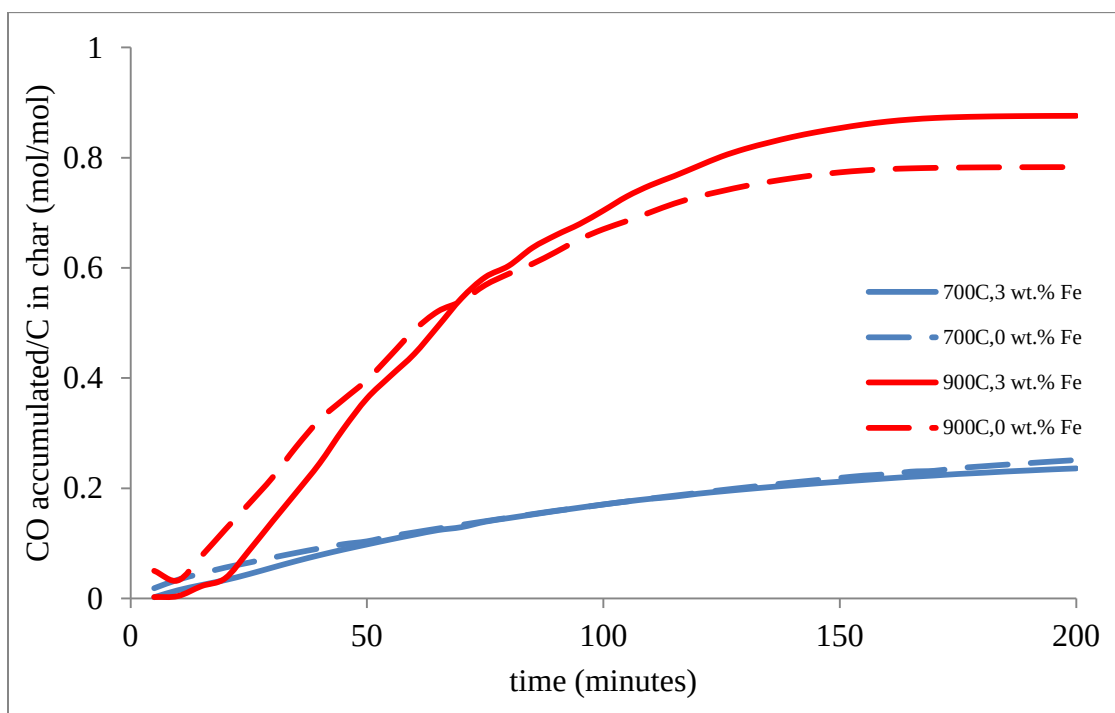


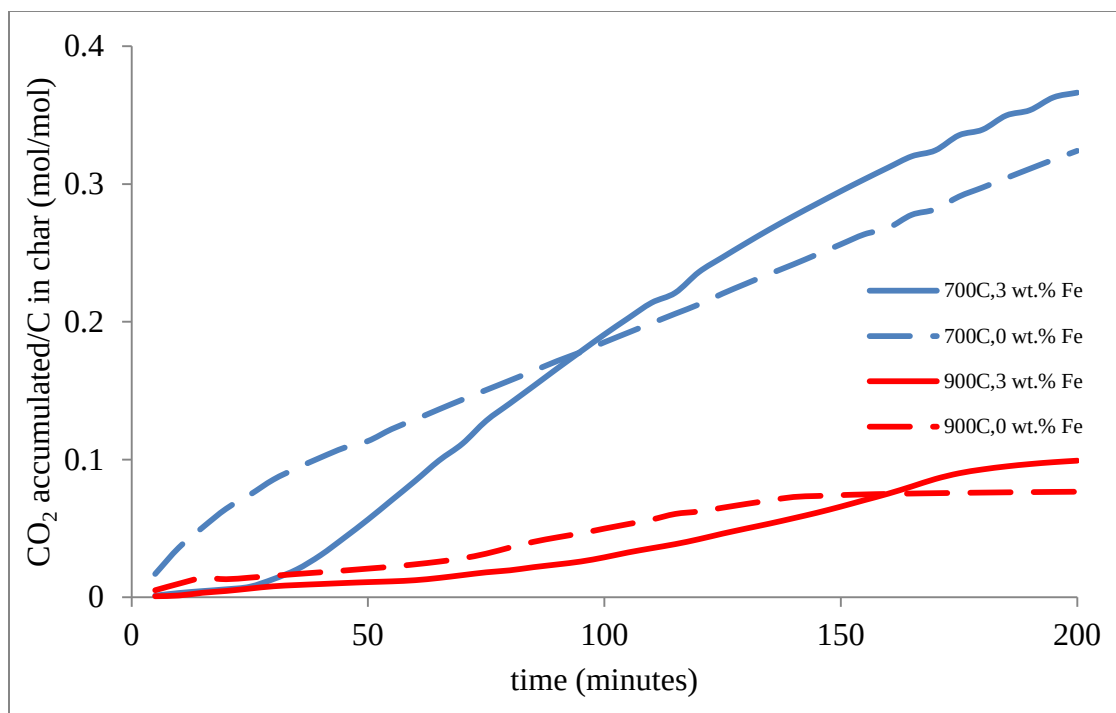
Figure 11



a)



b)



c)

Figure 12

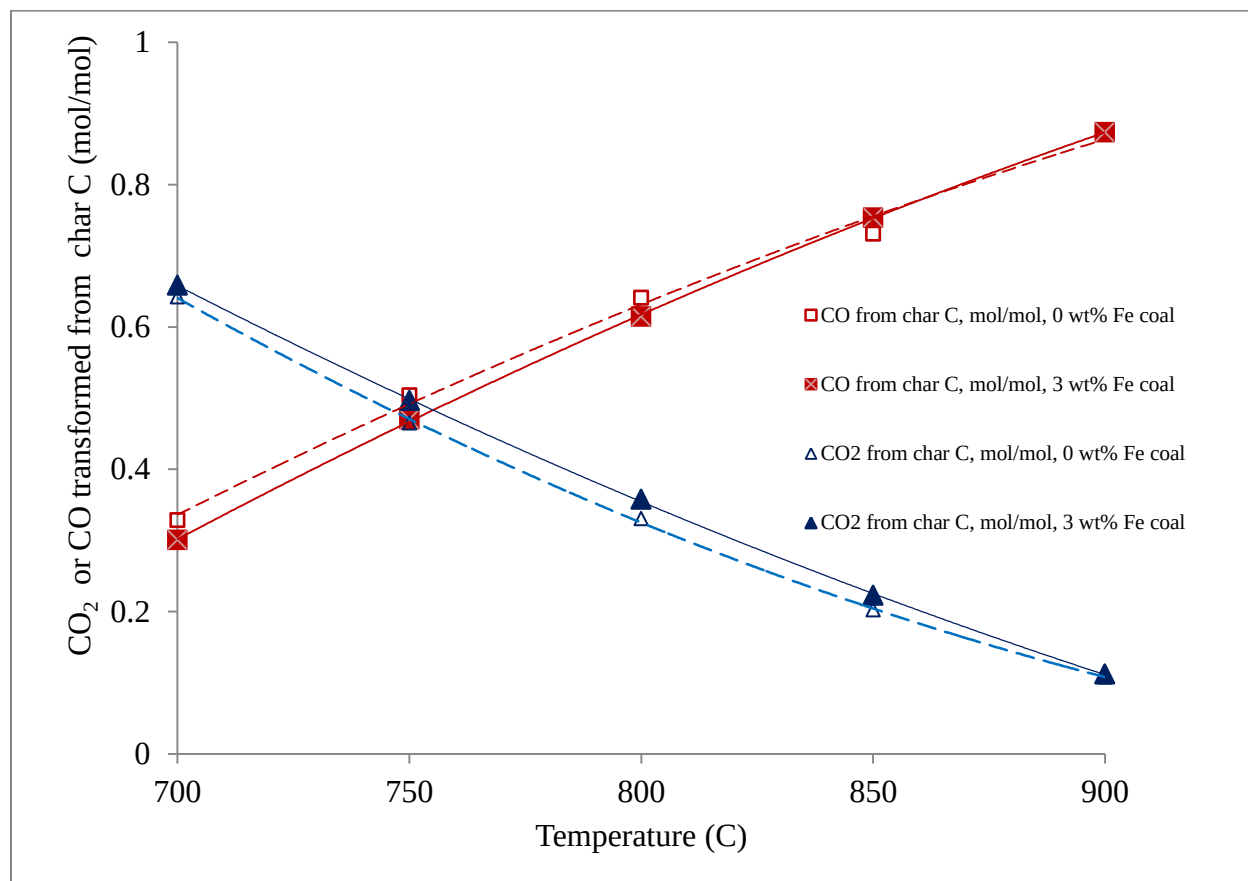


Figure 13

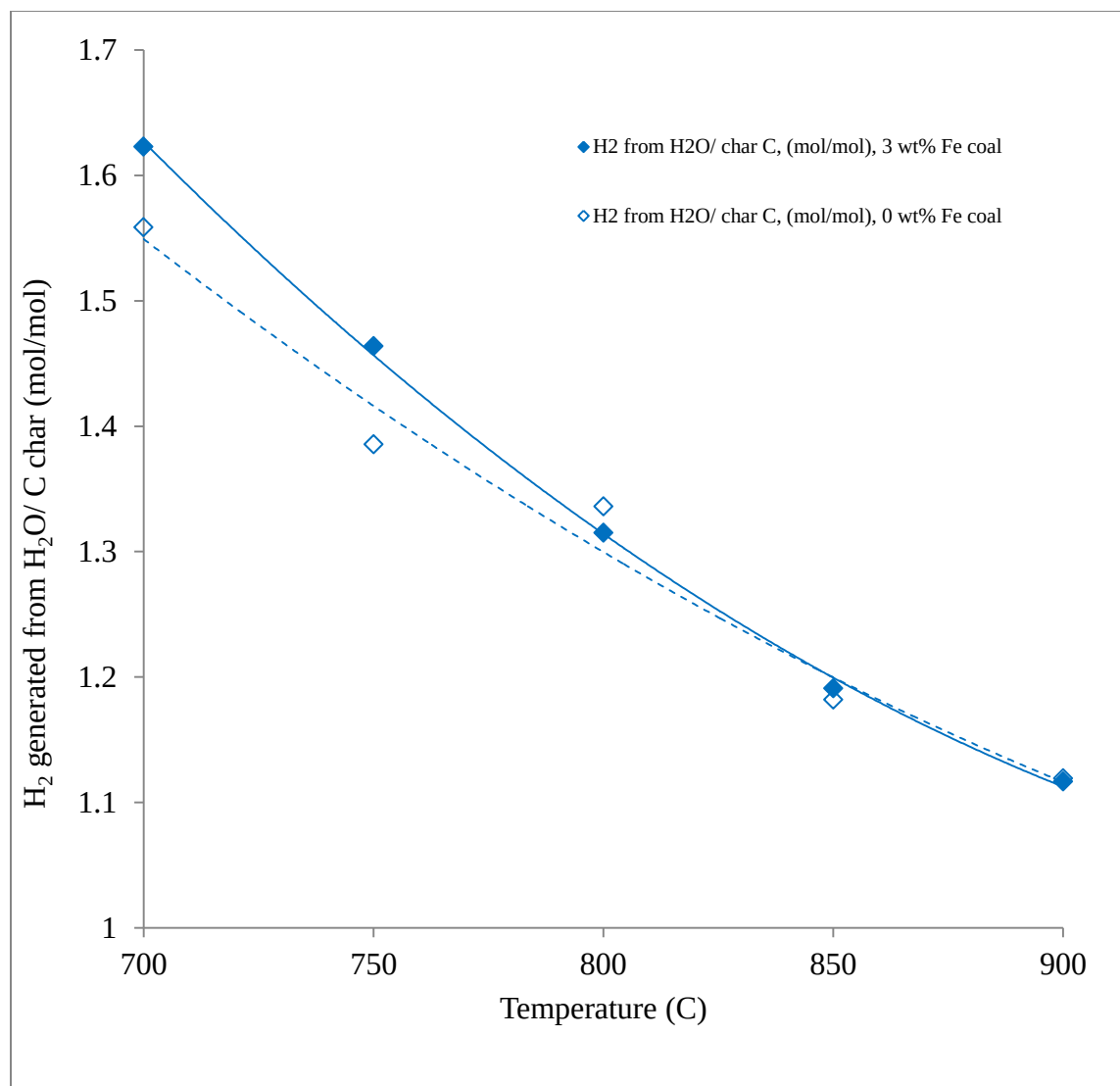


Figure 14

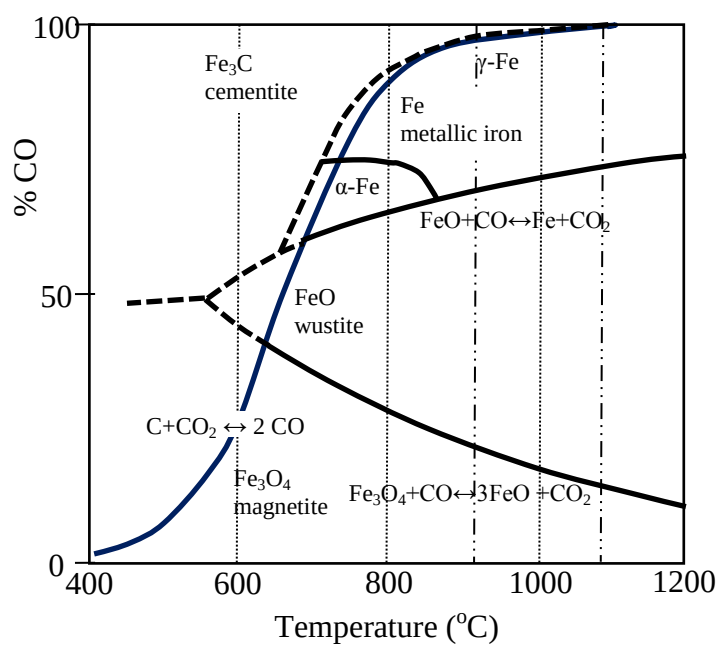


Figure 15

Table 1

Proximate Analysis	As Received (wt%)	Moisture Free (wt%)	DAF (wt%)
Moisture	20.87	-	-
Ash	5.86	7.41	-
Volatile matter	34.29	43.33	46.80
Fixed carbon	38.98	49.26	53.20
Total	100.00	100.00	100.00
Ultimate Analysis	As Received (wt%)	Moisture Free (wt%)	DAF (wt%)
Moisture	20.87	-	-
Hydrogen	2.46	3.11	3.36
Carbon	53.67	67.83	73.26
Nitrogen	0.89	1.12	1.21
Sulfur	0.42	0.53	0.57
Oxygen	15.83	20.00	21.60
Ash	5.86	7.41	-
Total	100.00	100.00	100.00
Heating Value, (Btu/lb)	9,255	11,696	12,632
(kJ/kg)	21,527	27,205	29,382

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

Table 2

Element	(wt%)	Oxide	(wt%)
Si	14.24	SiO ₂	31.77
Al	7.59	Al ₂ O ₃	14.97
Fe	4.23	Fe ₂ O ₃	6.31
Mg	3.83	MgO	6.62
Ca	18.73	CaO	27.33
Ti	0.6	TiO ₂	1.04
K	0.66	K ₂ O	0.83
P	0.51	P ₂ O ₅	1.22
Na	1.26	Na ₂ O	1.77
Mn	0.02	MnO ₂	0.04
Ba	0.35	BaO	0.41
Sr	0.41	SrO	0.51
S	2.76	SO ₃	7.19

Table 3

T°C	700	800	900
wt%			
Ash	22.82	27.13	30.62
C	71.06	68.47	66.31
H	0.78	0.53	0.5
N	0.65	0.65	0.65
S	0.65	0.67	0.83
O	4.04	2.55	1.09
Total	100	100	100

Table 4

Sample Temperature (K)		3% Fe Coal 295	Devol. 800C 295 80 4			Devol. 800C + 10 min H ₂ O 295 80 4		
Fe ⁵⁺	CS		-0.06	0.03	0.04	-0.10	0.08	0.07
	QS		0.15	0.02	0.03	0.13	0.08	0.33
	Width		0.65	0.63	0.60	0.42	1.47	1.10
	Area		43	42	40	28	40	37
Fe ³⁺ Nanophase oxide?	CS					0.58	0.17	0.07
	QS					0.80	-0.09	0.31
	Field						341.1	336.0
	Width					1.16	1.19	1.20
	Area					24	21	13
Fe ³⁺ Nanophase oxide?	CS		0.41	0.37	0.33			
	QS		1.15	0.00	-0.03			
	Field			489.8	258.6			
	Width		0.44	1.39	0.32			
	Area		7	11	15			
Cementite	CS		0.16	0.32	0.11			
	QS		-0.02	-0.02	0.00			
	Field		214.9	253.2	345.8			
	Width		0.31	0.36	0.29			
	Area		18	17	29			
Metallic iron	CS		-0.01	0.11	0.48	0.00	0.08	0.15
	QS		0.02	-0.01	-0.21	0.01	0.08	-0.09
	Field		338.4	345.4	501.9	338.3	349.8	346.8
	Width		0.31	0.31	1.04	0.34	1.31	0.89
	Area		32	31	16	40	25	29
FeOOH	CS					0.68	0.45	0.47
	QS					-0.13	0.00	-0.05
	Field					461.0	489.3	508.1
	Width					0.70	1.37	1.14
	Area					9	15	21
Hematite	CS	0.49						
	QS	-0.05						
	Field	498.6						
	Width	0.36						
	Area	20						
Hematite	CS	0.27						
	QS	-0.06						
	Field	501.8						
	Width	0.54						
	Area	68						
Hematite	CS	0.38						
	QS	-0.09						
	Field	518.6						
	Width	0.23						
	Area	12						
	χ^2	947.9	609.5	1379.8	1573.0	602.3	468.3	334.1
	χ^2_{norm}	1.8	1.2	2.7	3.0	1.2	0.9	0.7

CS = isomer shift, in mm/s. QS = quadrupole splitting, in mm/s. Field is magnetic field in kOe. Width = FWHM of peaks. Area is percentage of total spectral area.

Table 5

	Temp.	H ₂ from H ₂ O produced	CH ₄ produced	CO produced	CO ₂ produced
wt%. Fe	°C	mol/mol C	mol(*10 ⁻²) /mol C	mol(*10 ⁻¹) /mol C	mol (*10 ⁻¹) /mol C
0	700	1.558	3.739	3.285	6.424
0	750	1.386	3.086	5.040	4.651
0	800	1.336	2.830	6.410	3.305
0	850	1.182	2.286	7.308	2.024
0	900	1.119	1.720	8.746	1.081
3	700	1.623	3.813	3.007	6.584
3	750	1.464	3.307	4.702	4.967
3	800	1.315	2.776	6.145	3.577
3	850	1.191	2.287	7.536	2.230
3	900	1.117	1.329	8.73	1.120