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Influence of Pyrolysis Gas on Volatile Yield and CO₂ Reaction Kinetics of the Char Samples Generated in a High-Pressure, High-Temperature Flow Reactor

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Abstract: The influence of pyrolysis atmosphere on volatile yield, structural characteristics, and CO₂ reaction kinetics have been examined on chars generated from Pittsburgh No. 8 coal at 6.2 bar pressure and 1100 °C in a high-pressure, high-temperature flow reactor (HPHTFR) in Ar, N₂, 50 (vol. %) CO₂ and N₂ (i.e., CO₂/N₂) atmospheres. The chars were characterized for volatile yield, thermal swelling ratio, surface area, pore size distribution, crystallite structure, defects to graphitic intensity ratio, and char-CO₂ reactivity. Coal pyrolyzed in CO₂/N₂ showed higher volatile yield (27%) compared to coal pyrolyzed in argon (~16%) and nitrogen (~19%). Except for volatile yield, there was no significant difference in structural properties for chars generated in different pyrolysis atmospheres. The difference in volatile yield was found to be due to presence of unconverted tetrahydrofuran (THF) soluble tar/soot. The results also showed that the intrinsic reactivity was highest for char generated in N₂ atmosphere and lowest for char generated in CO₂/N₂ atmosphere. The kinetic parameters (activation energy and pre-exponential factor) for the char-CO₂ reaction were ascertained using nth order model. The activation energies did not differ significantly among the chars generated in different pyrolysis atmospheres. The order of reaction was found to follow: CO₂/N₂ char > N₂ char ≈ Ar char.

Keywords: gasification; pyrolysis atmosphere; kinetics; high pressure; high heating rate

1. Introduction

Integrated gasification combined cycle (IGCC) is one of the advanced technologies that has potential to reduce coal's carbon footprint. The heart of the IGCC plant is the gasifier where the organic portion of the coal is converted into syngas (i.e., primarily CO+H₂), while the inorganic portion of the coal is removed as slag. The syngas thus produced can not only be used for power generation but also as input to fuel cells or as a base to chemicals and liquid fuel synthesis [1]. Despite many commercial operations for various applications, gasification rates at high pressures and temperatures, crucial to the design and troubleshooting of the gasifiers, are relatively unknown [1].

When coal is exposed to high temperatures, it releases volatiles quickly to form char. The char particles thus generated get converted to syngas through heterogeneous reactions with CO₂ and H₂O. The heterogeneous reactions being slowest determine the overall gasification kinetics. The gasification kinetics in an entrained flow gasifier is not only dependent on intrinsic kinetics of the char reacting with CO₂, but also on the char properties such as pore structure, morphology, and char surface

area. The intrinsic kinetics, and char properties are usually determined using chars generated in an inert environment (or pyrolysis) by matching as many conditions as an entrained flow gasifier. It is important to note that the devolatilization (i.e., char generation) in an entrained flow gasifier happens in presence of reacting gases such as CO_2 and H_2O . The question that needs to be asked is how the pyrolysis gas environment affects volatile yield (i.e., amount of volatiles released during pyrolysis), char properties, and kinetics in a high-pressure condition? Earlier studies have reported high pressure reactivity of chars and the experiments were conducted either in an inert atmosphere, or in the presence of reacting gases [2–9]. The effects of pyrolysis atmosphere on volatile yield, and char characteristics at atmospheric pressure conditions were reported by several researchers [10–12]. Rathnam et al. [10] examined the volatile yield of four pulverized coals during pyrolysis in CO_2 and N_2 atmospheres. The experiments showed that the volatile yields in CO_2 atmosphere were 4–24% higher compared to N_2 atmosphere. The authors attributed the higher volatile yield in CO_2 atmosphere to gasification. This observation contradicts the findings of Borrego and Alvarez where the volatile yield of two bituminous coals decreased by about 60% and 30% when N_2 was replaced by CO_2 during experiments in a drop tube reactor at 1300 °C [11]. Brix et al. attributed this unusual observation to high volumetric flow rate of cold gas reducing the particle heating rate when using higher thermal capacity CO_2 as compared to lower thermal capacity N_2 . Brix et al. studied the effect of gas atmosphere on the char morphology, surface area, and volatile yield of a bituminous coal during pyrolysis in CO_2 and N_2 atmospheres at 1400 °C in a drop tube reactor [12]. Interestingly, the authors observed no effect of pyrolysis atmosphere on char morphology, volatile yield, and surface area. More recently, Wang et al. studied the effect of simulated pyrolysis gas (containing CO_2 , CO , H_2 , CH_4 , and N_2) on char reactivity and characteristics of a Chinese bituminous coal using a bubbling fluidized bed reactor [13]. The temperatures used in the study were between 450 to 600 °C and the residence time of the particles was kept at 15 min. Under these conditions, the authors observed that the pyrolysis atmosphere had no significant effect on char morphology but noted the pyrolysis atmospheres affected the char reactivity in CO_2 and H_2O atmospheres. It must be recognized that in this temperature range, the heating rate would be less than 100 °C/s and that does not reflect the heating rate and temperature experienced by the particles in an entrained-flow gasifier. However, from the short review, it is apparent that, the effects of pyrolysis gas atmosphere on volatile yield and intrinsic reactivity with CO_2 or H_2O are not conclusive. While steam is an important reactant in the slurry-fed entrained flow gasifier, this study restricts to three pyrolysis gases: N_2 , Ar, and CO_2/N_2 . This is due to instrument limitation in feeding slurry to the reactor. This investigation focuses on: (1) determining the volatile yield of chars generated in various pyrolysis atmospheres at elevated pressure and (2) determine the CO_2 reactivity of chars generated in various gas atmospheres.

2. Material and Methods

2.1. Coal Preparation

A widely used bituminous coal, Pittsburgh No. 8 coal, was used for this study. The coal was prepared by dry grinding method in an industrial rod mill. The ground coal was sieved between 100 and 140 ASTM (American Society for Testing Materials) meshes and stored in an Ar filled aluminum bag. The particle size fraction of $-150+106\ \mu\text{m}$ was chosen as it covers about 10% of the feed to a typical commercial slurry-fed entrained-flow gasifier. The properties of the coal are shown in Table 1. The methodology employed to generate proximate and ultimate analyses data is described in the “char characterization” section.

2.2. Char Preparation

All the experiments were conducted in an electrically heated HPHTFR. The reactor is capable of reaching a maximum temperature of 1650 °C and 30 bar pressure. The schematic of the reactor is shown in Figure 1. The same reactor, used at atmospheric pressure, is described in detail elsewhere [14,15].

The reactor consists of a feeder, a high temperature furnace, a sample collection section, and a gas analysis section. The high temperature furnace section consists of a high alumina ceramic (reaction) tube (65 mm i.d $\times$ 700 mm long) with a mullite flow straightener (honeycomb) placed at the top surrounded by six super Kanthal heating elements, all encased in a refractory-casted, lined carbon steel pressure vessel. The concentric section between the refractory wall and the outer surface of the reaction tube was used to preheat secondary gas. The secondary gas, composed of CO₂ and N₂, constituted the majority of the gas (~90%) flowing into the reactor. Inert gas was used as the primary gas to transport particles from the feeder to the reaction zone. The gases were supplied by gas cylinders, and the flow rates were controlled by calibrated mass flow controllers. The reactor temperature was continuously monitored by a thermocouple placed close to the outer surface of the ceramic tube around the mid-section. Once the desired temperature was achieved, the reactor was purged with the reaction gas for a few minutes. After which the reactor pressure was increased using a back-pressure regulator. The gas was allowed to flow for about 10–15 min at the desired pressure until the gas composition exiting the reactor, monitored using a calibrated micro gas chromatograph reached the inlet gas composition.

After reaching the inlet gas composition, a sample of about 30 to 45 g was fed into the reactor at a stable feed rate of 3.00 ± 0.02 g/min. To ensure the flow was laminar in the reactor, a flow straightener was placed at the top of the ceramic tube. The values of Reynolds number ranged from 480 to 730. As the critical number for transitioning into the turbulent region is 2300, it is safe to say that all the experiments were conducted in the laminar flow regime. The ceramic tube wall temperature was maintained at 1100 °C, which is on the lower side of the operating temperature of a typical slurry-fed entrained-flow gasifier. The lower temperature was chosen to avoid significant difference in conversion between chars generated in inert atmosphere and reaction gas atmosphere. The summary of experimental conditions maintained in the reactor to generate chars is shown in Table 2.

Upon injection of the sample into the reactor, the particles devolatilize/react as they pass through a 0.60 m reaction zone to form char-ash particles. The particle residence time was determined by solving force balance equation for particle velocity assuming uniform gas velocity [16]. The particle residence time for a 125 μ m particle was calculated to be ~2.3 s. The char-ash particles collected through the water-cooled probe were captured by a series of filters with the last filter having a mesh opening of 1 μ m. The resulting product gas exited the filter below 60 °C and was further cooled in a heat exchanger to remove any remaining moisture before being analyzed for components via micro gas chromatography. The char sample, contaminated with soot, was collected in the filter and used for further analysis. The study investigated raw char sample obtained from the HPHTFR as well as studying the THF washed HPHTFR char to remove the effects of tar and soot on reactivity. The methodology employed in this investigation is shown in Figure 2.

Table 1. Coal properties.

Coal	Pittsburgh No. 8 Coal
Particle size fraction	−150 + 106 μm
Proximate analysis (dry basis, weight %)	
Volatile Matter	38.0
Fixed Carbon	54.7
Ash	7.3
Ultimate analysis (dry basis, weight %)	
Carbon	82.2
Hydrogen	5.4
Nitrogen	1.6
Sulfur	1.5
Oxygen	2.0
Calorific Value, MJ/kg	34.0

Table 2. Experimental conditions.

Pyrolysis Gas Atmosphere in the Reactor	Primary Stream		Secondary Stream		Maximum Reactor Tube Wall Temperature/Pressure *
	Gas	Flow Rate (SLPM)	Gas	Flow Rate (SLPM)	
N ₂	N ₂	6	N ₂	48	1100 ± 7 °C/6.2 bar
Ar	Ar	6	Ar	48	1100 ± 7 °C/6.2 bar
50 vol.% CO ₂ and 50% N ₂ or (CO ₂ /N ₂)	N ₂	6	CO ₂ and N ₂	CO ₂ (27) and N ₂ (21)	1100 ± 7 °C/6.2 bar

* Absolute pressure; SLPM is standard liters per minute.

2.3. Char Characterization

2.3.1. Proximate Analysis

Proximate analysis of chars was carried out in a Leco MAC 400 analyzer. Approximately 0.1–0.2 g of sample was crushed in a pestle and mortar before analysis. Moisture, volatile matter, ash, and fixed carbon were obtained. Table 3 presents the proximate analyses of the chars obtained from the HPHTFR. Based on the proximate analyses data, the volatile yield (for pyrolysis in N₂, and Ar) or conversion (during gasification in CO₂/N₂) was determined using ash as the tracer using following equation:

$$\% \text{ Conversion (or volatile yield)} = \frac{10000 \times (A_1 - A_0)}{A_1 \times (100 - A_0)} \quad (1)$$

where A₁ and A₀ are the ash content of char and coal on dry wt. % basis, respectively. The term volatile yield will be used in the text to refer to conversion of the char generated in the CO₂/N₂ atmosphere.

2.3.2. Thermal Swelling Ratio

The thermal swelling ratio of the chars was determined by the procedure explained by Fletcher et al. [17,18]. The apparent density of the chars and coal sample was determined using the tap density technique assuming the packing factor of coal sample and char to be the same. The apparent density ratio ($\frac{\rho_{po}}{\rho_p}$) and weight loss data were then related to the swelling ratio (d/d_o) by:

$$\frac{d}{d_o} = \left(\frac{\rho_{po}}{\rho_p} \times \frac{m}{m_o} \right)^{\frac{1}{3}} \quad (2)$$

where, d/d_o represents swelling ratio. The subscript “o” refers to parent coal and without it refers to char. The mass ratio m/m_o in the equation is expressed on an as-received basis. The density ratio ρ_p/ρ_{p0} refers to the ratio of apparent densities, where apparent density is defined as the mass of a particle divided by the total volume enclosed by the outer surface of the particle (assumed to be spherical). The bulk or bed density (ρ_p for the char and ρ_{po} for the coal) is measured using the tap technique.

Table 3. Proximate analysis of the chars generated in different pyrolysis atmospheres.

Pyrolysis Atmosphere	VM _d , wt. %	FC _d , wt. %	Ash _d , wt. %
Before washing with THF			
Argon	23.5	67.9	8.6
Carbon dioxide/Nitrogen	19.3	71.0	9.7
Nitrogen	25.7	65.4	8.9
After washing with THF			
Argon	20.9	69.1	9.8
Carbon dioxide/Nitrogen	20.4	69.7	10.0
Nitrogen	20.0	70.1	9.9

Subscript “d” represents dry basis; VM: Volatile matter; FC: Fixed carbon.

Figure 1. Schematic of the high-pressure, high-temperature flow reactor.

2.3.3. Surface Area Analysis and Pore Size Distribution

The chars were degassed at 150 °C for a period ranging between 4 to 10 h in vacuum. Total surface area and pore size distribution of degassed chars were determined using N₂ adsorption-desorption isotherms at 77 K. The isotherms were analyzed using the Brunauer–Emmett–Teller (BET) equation to calculate total surface area, and Barrett–Joyner–Halenda (BJH) analysis to calculate pore size distribution.

2.3.4. Raman Spectra

Raman spectra of chars were obtained with an excitation laser at 532 nm using Horiba Confocal Raman microscopy. Particles of each sample were placed on a slide and were focused using a 50X objective lens. The laser power on the char surface was controlled approximately at 5 mW. Scans from

800 cm^{-1} to 2300 cm^{-1} were performed on each sample. Resolution was approximately 1 cm^{-1} , and the acquisition time for each spot was 60 s. The laser spot diameter reaching the sample was 5 μm . The spectra of at least 10 different spots were obtained for every sample. The ratio of defects to graphite band was obtained, averaged, and the error bar was determined using t-distribution with 95% confidence interval.

Figure 2. Methodology employed in this investigation.

2.3.5. X-ray Diffraction

X-ray diffraction analyses were performed using a PANalytical instrument equipped with a 45-kW high-intensity rotating anode ($\text{Cu K}\alpha$ radiation, 1.5406 $\text{\AA}$, 0.02°/step, 225 s/step). The analyses were performed on finely ground thin powder samples of the coal chars mounted on a zero-background quartz holder. Measurements were recorded from a start angle $2\theta = 10^\circ$ to an end angle of 70° . The XRD patterns were analyzed for the Full Width Half Maximum (FWHM) using JADE software. From the FWHM, the structural parameters were obtained using conventional Scherrer equations given by:

$$L_a(\text{\AA}) = \frac{1.84\lambda}{B_a \cos\theta_a} \quad (3)$$

$$L_c(\text{\AA}) = \frac{0.9\lambda}{B_c \cos\theta_c} \quad (4)$$

where, L_a is the lateral size and L_c is the stacking height of the crystallite, λ is the wavelength of the radiation used, B_a and B_c are the FWHM of the (100) and (002) peaks, respectively, and θ_a and θ_c are

the corresponding scattering angles. The FWHM is a strong function of the background curve fitting. In order to ensure the validity of the data, the FWHM was obtained by repeating the procedure three times and an error bar was obtained using the t-distribution.

2.4. Tar/Soot Removal and Analysis

The removal of tar/soot from char was done by washing the sample with tetrahydrofuran (THF). THF can be used to remove tar [19] and is known to provide greater extractability of coal tar without altering the characteristics [20]. To extract the tar/soot from char, a small amount (~0.5 g) of char was added to 100 mL of tetrahydrofuran and allowed to stand for about 15 min followed by heating it to its boiling point (i.e., 66 °C). The boiling slurry was filtered to remove the char sample, while the tar/soot dissolved in THF was concentrated by vaporizing THF in vacuum. The THF soluble tar/soot was analyzed in an Agilent 7890A Gas Chromatograph (GC) and 5975C Mass Spectrometer (MS) mounted with HP-5ms (length 30 m, diameter 250 µm, and film thickness 0.25 µm) column. Sample was injected at 280 °C with a gas flow of 1 mL/min (STP). The transfer line between the GC and the MS was held at 300 °C. The MS spectra were acquired in scan mode in the range 40–500 µm. The THF washed char sample was dried in a vacuum oven at 60 °C and 25 in Hg vacuum for over 12 h.

2.5. Char Reactivity

Reactivity of chars, obtained from the HPHTFR, was measured using an High Pressure Thermogravimetric Analyzer (HPTGA). All the TGA experiments were conducted at 6.2 bar. A small amount of char sample (~35 mg) was heated to 900 °C and 6.2 bar in Ar atmosphere and held at that temperature for 15 min to remove any volatiles. In all cases, the weight loss curve reached an asymptote before 15 min. The system temperature was brought down in Ar atmosphere (i.e., 825–875 °C) at which the gas atmosphere was switched to CO₂ and the conversion was measured by weight loss. The flow rates of the reaction gas during the isothermal step as well as the inert gas (i.e., Ar) during temperature ramp-up step were maintained at 0.41 SLPM. The typical data obtained from the HPTGA takes the form of weight loss versus time. The data were smoothed using regression in Microsoft excel. The isothermal gasification step was then normalized assuming the char was at 0% conversion and conversion percent (X) on dry ash-free basis versus time was obtained by:

$$X (\%) = \left(\frac{m_o - m_t}{m_o} \right) \times 100 \quad (5)$$

where m_o and m_t are the mass of dry ash-free char present at the beginning ($t = 0$) of the isothermal gasification step and at time t , respectively.

From the weight loss curves, the apparent reaction rate (R_{app}) was calculated by:

$$R_{app} (\text{gg}^{-1} \text{min}^{-1}) = \frac{1}{m_i} \times \left(\frac{d_m}{d_t} \right) \quad (6)$$

where m_i is the sample mass (dry ash-free basis) remaining at reaction time t . Apparent reaction rate is a function of intrinsic char reactivity and reactive surface area. The intrinsic reaction rate is the rate measured free of mass transfer restrictions (under kinetic controlled regime), expressed as $\text{gm}^{-2} \text{min}^{-1}$. The intrinsic reactivity was calculated by normalizing the apparent reactivity with BET surface area by:

$$R_{\text{int},10\% \text{ conv}} (\text{gm}^{-2} \text{min}^{-1}) = \frac{R_{app}}{SA_{10\% \text{ conversion}}} \quad (7)$$

Expressing the rates as intrinsic reaction rates allows comparison of reaction rate measurements of physically different samples having different surface areas.

The reaction rate was related to temperature and partial pressure at specified conversion using Equation (6):

$$R_{app}(\text{gg}^{-1}\text{s}^{-1}) = A_0 \exp\left(\frac{-E_a}{RT_p}\right) P_{\text{CO}_2}^n \quad (8)$$

where, R_{app} is the measured reaction rate ($\text{gg}^{-1}\text{s}^{-1}$), E_a is the measured activation energy (kJ mol^{-1}), A_0 is the pre-exponential factor, R is the universal gas constant ($\text{J K}^{-1} \text{mol}^{-1}$), T_p is the particle temperature (K), P_{CO_2} is the partial pressure of CO_2 (in bar), and n is the reaction order.

The activation energy is obtained from the slope of the plot of $\ln R_{app}$ vs. $1/T_p$. The intercept of the line represents the pre-exponential factor ($A = A_0 P_{\text{CO}_2}^n$), expressed as s^{-1} . Reaction orders with respect to CO_2 were determined by measuring reaction rates at various CO_2 partial pressures (25, 50, and 100% of the total pressure). The reaction order was obtained from the slope of the plot $\ln R_{app}$ vs. P_{CO_2} .

Reaction rates measured at 10% conversion, instead of 0% conversion, were used in calculating kinetic parameters. This was done to avoid fluctuations in temperature and gas composition during transition from Ar to CO_2 .

For high pressure chars, it is not reasonable to assume that the surface area of the chars at 10% conversion is the same as the initial char surface area. Therefore, the surface area was obtained at $10 \pm 2\%$ conversion of char during the isothermal step in the HPTGA. For the sake of clarity in discussion, the char obtained at $10 \pm 2\%$ conversion in the HPTGA will be discussed as 10% converted char in the rest of the text.

3. Results and Discussion

3.1. Volatile Yield

The effect of pyrolysis atmosphere on volatile yield (or conversion) was ascertained using ash as the tie component (i.e. tracer). The volatile yields were ranging from ~16% for the char pyrolyzed in Ar atmosphere to ~27% for the char obtained in the CO_2/N_2 atmosphere (shown in Figure 3). The differences in volatile yields for the char generated in CO_2/N_2 compared to the chars generated in other atmospheres are statistically significant given the standard deviation for the volatile yield in CO_2/N_2 was $\pm 1.8\%$. An atmospheric pressure study also observed higher volatile yield during pyrolysis in CO_2 atmosphere compared with N_2 atmosphere and attributed this increased volatile yield to gasification [10].

Figure 3. Volatile yield for chars generated in different pyrolysis atmospheres.

It is interesting to note that the volatile yield (or conversion) was lower than 38% (ASTM Volatile matter of $-150+106 \mu\text{m}$ particles) for pyrolysis. This might seem unusual as the temperature in the reactor was 1100°C ($>$ ASTM proximate analysis specifications). The unusual observation of lower volatile yield could be due to higher pressure (>1 bar) and lower residence time (~ 2.3 seconds) in the reactor for these chars compared to 7 min at atmospheric pressure and 950°C in ASTM volatile matter

determination. If pressure had played significant role in reducing the volatile yield (or higher residual volatiles in the char), it should also be reflected in the residual volatiles present in the char sample generated in a commercial gasifier. Analysis of char-slag sample collected from a particulate filter on a commercial gasifier showed >50% volatiles (on dry ash free basis) of the feed was present in the char [21]. This points to not all volatiles are removed during high pressure pyrolysis and confirms the reliability of the data obtained in the study. It was also suggested that at elevated pressures, the amount of volatiles released decreases due to increased mass transfer resistance [17]. The increased mass transfer resistance leads to deposition of tar and soot on the char particles. The difference in conversion could be due to the amount of tar/soot settled on the char particles. The presence of tar and soot with char particles generated at elevated pressures were also reported by Shurtz and Fletcher [4]. The tar/soot present in each char sample was partially removed by washing the sample in THF. The conversion was also determined after chars were washed in THF. The conversion for the char generated in the CO₂/N₂ atmosphere increased marginally from 27 to 29%, while the conversion for chars generated in N₂ and Ar atmospheres increased from 19% to 29% and 16% to 28%, respectively. The significant increase in conversion after washing with THF for chars generated in N₂ and Ar indicates the THF soluble tar and soot were not consumed in the HPHTFR, while these components were converted in the presence of CO₂ in the HPHTFR as shown by a smaller increase in conversion after washing with THF.

3.2. Surface Area, Pore Size Distribution and Swelling Ratio

Although the primary focus of this study is to measure the volatile yield during pyrolysis, and to determine the kinetics of chars generated in different atmospheres, the results of surface area, pore size distribution, and swelling ratio are also presented to determine the difference in structural features.

The chars were analyzed for BET surface area and BJH pore size distribution measurements and the results are as follows: The surface area of chars generated in CO₂/N₂, N₂, and Ar were 9.5 ± 0.2, 6.5, and 6.3 m²/g, respectively. After washing with THF, the surface areas of chars pyrolyzed in CO₂/N₂ and N₂ were almost the same at 8.5 and 8.7 m²/g, respectively. All these show that pyrolysis atmosphere does not substantially affect the initial surface area of the chars.

The other factor that can affect the kinetics is the morphology of the chars. A char that underwent higher swelling is more likely to fragment during gasification [22]. Increased fragmentation affects the char particle size distribution in the gasifier and that affects the kinetics and particle residence time. From that perspective, swelling ratio of the chars was examined by measuring the apparent density using a tap density technique. The swelling ratios of chars generated in the CO₂/N₂, N₂, and Ar atmospheres were found to be 1.70, 1.74, and 1.72, respectively (shown in Table 4).

Table 4. Thermal swelling ratio of chars.

Gas Atmosphere	Before THF Washing	After THF Washing
CO ₂ /N ₂	1.70 ± 0.006	1.69
N ₂	1.74 ± 0.004	1.63
Ar	1.72 ± 0.005	1.65

Similarities in swelling ratio can also be due to the presence of tar and soot with char. The soot particles collected from the reactor were large agglomerates with extremely low density. Presence of low-density soot particles and tar with char can lower the density of the char sample and consequently increase the swelling ratio. Therefore, the swelling ratio of the THF washed chars was also determined. After washing with THF, the char generated in CO₂/N₂ showed slightly higher swelling ratio of 1.69 compared to 1.65 and 1.63 for chars generated in N₂ and Ar atmospheres, respectively. The error bar in these measurements was ±0.005. The decrease in swelling ratio for the chars generated in N₂ and Ar can be attributed to removal of tar/soot and due to increased conversion, while the tar generated in CO₂/N₂ pyrolysis atmosphere got consumed.

3.3. Char Reactivity

It must be emphasized that the reactivity measured is not just char reactivity but also includes soot reactivity. There was a difficulty in quantifying and separating the soot from char. Although the reactivity measured is a combination of soot and char, only char reactivity will be referred to henceforth in the text for the sake of clarity in the discussion.

Figure 4 shows the char conversion profiles with CO₂ at 6.2 bar in the HPTGA. The temperature effect on conversion is straightforward where increase in temperature increased conversion (in daf basis) for all the chars. The apparent reaction rate was calculated and found to increase with increase in temperature for all the chars. The apparent reaction rate at 10% conversion at 875 °C followed the order: N₂ pyrolyzed char (0.0153 min^{−1}) > Ar pyrolyzed char (0.0136 min^{−1}) > CO₂/N₂ pyrolyzed char (0.0129 min^{−1}). The apparent reaction rate is affected by a combination of parameters such as physical properties (i.e., surface area and morphology) and chemical structure (i.e., structural ordering of carbon) [23]. As discussed earlier, the surface area (ranging between 6–10 m²/g) and the morphology (determined through the swelling ratio) of the chars were not substantially different. With the surface area being not too different, the reactivity difference is attributed to chemical structural differences.

The chars were analyzed by Raman spectroscopy for defects and graphitic regions to ascertain structural differences. A char with higher intensity of defects to graphite is expected to be structurally more reactive [24]. Interestingly, the ratios of the intensity of defects to graphite were also similar for chars generated in different atmospheres (shown in Figure 5). These results also did not explain the difference in reactivity of chars generated in different pyrolysis atmospheres. Since the Raman spectroscopy is a surface technique, the soot contamination might have affected the analysis. Therefore, the chars were characterized for the structural ordering of carbon using XRD, a bulk technique. The XRD patterns are shown in Figure 6. The lateral size of the crystallite L_a , and the stacking height of the crystallite L_c were obtained using (100) and (002) peaks, respectively. Since the crystallite dimension is a function of background curve of the XRD plot, the procedure for determining the crystallite dimensions was repeated thrice. The average L_a values for the chars ranged between 32–34 Å, with the lowest being 32 ± 3.1 Å for the char pyrolyzed in N₂ to the highest value of 34 ± 3.1 Å for the char generated in Ar. The range is far narrower for the stacking height (L_c) of the crystals and was between 13.1 ± 1 – 14.2 ± 1 Å. The difference in the crystal parameters was statistically insignificant to conclude that pyrolysis atmosphere affected the lattice structure.

Figure 4. Cont.

Figure 4. Cont.

Figure 4. Conversion profiles of chars with CO₂ in HPTGA (The temperature in the legend indicates the HPTGA temperature and the gas atmosphere indicates the pyrolysis atmosphere in a high-pressure, high-temperature flow reactor (HPHTFR)).

Figure 5. The ratio of defects band intensity to graphite band intensity (I_d/I_g) (measured on chars before washing with tetrahydrofuran (THF)).

The other possibility for the difference in reactivity could be due to physical and chemical transformations that occurred either during the pyrolysis stage (i.e., the ramp-up stage in the HPTGA) or the gasification stage (i.e., the isothermal stage) in the HPTGA. To ascertain the transformations during the pyrolysis stage in the HPTGA, the chars generated in the N₂ and CO₂/N₂ atmospheres were heated to 875 °C in 6.2 bar pressure. The chars were maintained at 875 °C for about 15 min and cooled down. The surface area of the chars pyrolyzed in N₂ and CO₂/N₂ after the ramp-up stage was 19.8 and 22.3 m²/g, respectively. This difference in surface area also does not warrant significant difference in reactivity. This was followed by analyzing the surface area of the chars gasified in CO₂ atmosphere at 875 °C and 6.2 bar in the high pressure TGA. The reaction was stopped at 10 ± 2 % conversion and the chars were analyzed for surface area. Interestingly, the char generated in CO₂/N₂ showed the highest surface area of 155 ± 7 m²/g, followed by the chars generated in N₂ and Ar atmospheres at 113 ± 6 m²/g and 104 m²/g, respectively. Higher surface area for the CO₂/N₂ char can be attributed to increased generation of finer pores (pore width <30 Å). This was reflected in ~30%

lower pore volume for the char generated in N_2 compared to the char generated in CO_2/N_2 (shown in Figure 7). Although the difference in surface area is significant, the increased surface area for the char pyrolyzed in CO_2/N_2 did not result in higher reactivity (shown in Figure 8). This implies that the structure of the char generated in CO_2/N_2 is intrinsically less reactive compared to the char generated in inert atmospheres. The intrinsic reactivity of the char generated in CO_2/N_2 is ~62% and ~64% of intrinsic reactivities of the chars generated in N_2 and Ar, respectively (shown in Figure 9). Interestingly, XRD data (shown in Table 5) on the 10% converted char also did not show significant difference in lattice parameters. These further confirm that the approach used (i.e., Raman spectroscopy and XRD) to determine the structural differences are not adequate. The other noteworthy observation is the ~20% higher pore volume in the macropore region ($>500 \text{ \AA}$) for chars generated in inert atmospheres over the char generated in CO_2/N_2 . It appears that macropores provided access to feeder pores that may have resulted in higher reactivity.

Figure 6. XRD pattern of chars generated in different pyrolysis atmosphere (before washing with THF).

Table 5. Values of L_a and L_c for chars (before washing with THF).

Pyrolysis Atmosphere in HPHTR	Initial Char		10% Converted Char	
	L_a (Å)	L_c (Å)	L_a (Å)	L_c (Å)
CO_2/N_2	33.1 ± 3.1	13.7 ± 2.8	37.3	14.5
N_2	32.1 ± 2.2	13.1 ± 1.0	37.6	13.8
Ar	33.8 ± 1.5	14.2 ± 1.5	40.2	14.2

* Error bar was calculated based on t-distribution.

Figure 7. Pore size distribution of chars.

Figure 8. Apparent reactivity of chars before and after washing with THF (at 875 °C).

Figure 9. Intrinsic reactivity of chars generated in various pyrolysis atmospheres.

It can be hypothesized that higher reactivity for chars pyrolyzed in N₂ and Ar may be due to products formed from the highly reactive tar components on the char surface, which were not released completely during the temperature ramp-up stage in the HPTGA. The hypothesis was based on the observation that only about 65–80% of the volatiles, as determined by the proximate analysis, was released during the pyrolysis stage in the HPTGA. To remove the effects of tar/soot captured on the particle surface, chars were washed with THF before analyzing for CO₂ reactivity. Interestingly, the apparent CO₂ reactivity of the sample pyrolyzed in N₂, after washing with THF, decreased by ~25% at 875 °C, while the apparent reactivity of the sample pyrolyzed in Ar and CO₂/N₂ decreased by ~11% each at the corresponding temperature (shown in Figure 8). The difference in apparent reactivity for chars washed in THF is also far narrower ranging from 0.0115 min⁻¹ for the THF washed CO₂/N₂

char to 0.0122 min^{-1} for the THF washed N_2 char. To further confirm if this decrease in reactivity was only due to removal of tar/soot and not due to THF, a calcined coke was washed in the THF and dried using the same procedure employed to wash coal chars. The CO_2 reactivities of calcined petcoke and THF washed calcined coke were ascertained at 875°C and 6.2 bar. The reactivities showed no significant difference confirming that the THF had no effect on the reactivity of these samples (shown in Figure 10). After washing with THF, the apparent reactivities of chars were similar (shown in Figure 8). It is adequately shown that chemical structural differences among chars due to pyrolysis atmosphere, based on XRD and Raman techniques, proved to be inconclusive. At 10% conversion in the HPTGA, the char generated in CO_2/N_2 yielded higher surface area, higher pore volume, and almost similar apparent reaction rate as the 10% converted char generated in the N_2 atmosphere. The intrinsic reactivity of the THF washed char generated in N_2 decreased more compared to the char generated in CO_2/N_2 . The decrease in intrinsic reactivity of the char can be attributed to removal of tar and soot. For the char generated in CO_2/N_2 , the intrinsic reactivity dropped marginally owing to limited amount of extractable tar and soot.

The difference in reactivity before and after washing with THF was shown to be due to tar and soot. To determine the composition of tar and soot that contributed to increased reactivity, the THF soluble was analyzed in the GC-MS. The GC-MS spectrograms and the compounds speciation obtained from chars pyrolyzed in N_2 and CO_2/N_2 are shown in Table 6 and Figure 11. Qualitative analysis of the tar and soot showed the presence of polyaromatic hydrocarbons (PAH) for chars generated in N_2 and CO_2/N_2 . Interestingly, naphthalene was not observed in the THF soluble tar, while it was one of the major tar components obtained during gasification of Pittsburgh No. 8 coal char in CO_2 in atmosphere at 1300°C and 1 bar [25]. Higher concentration of polyaromatic hydrocarbons including a six-member ring compound (i.e., benzo(ghi)perylene) and absence of naphthalene suggest increased retrogressive reactions at higher pressure leading to polyaromatic condensation [26]. These PAHs must have acted as precursors to the product that contributed to differing reactivities for the chars generated in inert atmospheres. To determine the products from the tar/soot, the char generated in N_2 atmosphere was heated to 875°C at $10^\circ\text{C}/\text{min}$ in Ar atmosphere and was cooled in the HPTGA. The sample ($\sim 50 \text{ mg}$) was suspended in 35 mL of THF for 5 h and heated to 66°C . The filtrate was analyzed in the GC-MS. The filtrate showed no PAH confirming that tar compounds were completely decomposed to form higher molecular weight soot. The higher molecular weight soot must have been more reactive than the char itself.

Figure 10. CO_2 reactivity of the reference char and the THF washed reference char.

Table 6. Compounds identified by the GC-MS.

Retention Time (min)	Compounds	Area %	
		CO ₂ /N ₂	N ₂
10.70	1, 4 Benzene diamine, N,N'-bis (1-methyl ethyl)	4.4	2.3
10.95	2,5, cyclohexadiene-1,4-dione, 2,6-bis (1,1, dimethyl ethyl)	12.9	6.3
11.04	1 H cyclopropa(a)naphthalene	17.6	2.5
13.52	Phenanthrene	7.6	3.0
15.44	Fluoranthene	14.5	17.6
15.59	1,8, Anthracene diamine	0.0	2.5
15.69	Phenaleno (1,9-bc) thiophene	0.0	1.7
15.79	Pyrene	29.0	27.3
17.43 and 17.73	Cyclopenta (cd) pyrene	9.4	14.5
19.38/19.75	Benzo(k)fluoranthene	1.5	5.8
19.81	Benz(e)acephenanthrylene	1.3	5.7
21.71	Benzo(ghi)perylene	1.8	10.8
	Total	100	100

Figure 11. GC-MS chromatograms of THF soluble tars obtained by washing chars generated in CO₂/N₂ and N₂ atmospheres (only qualitative analysis).

3.3.1. Kinetic Parameters

The reaction rates versus conversion are shown in Figure 12. The kinetic parameters of the chars were obtained using the apparent reaction rate at 10% conversion. This was to avoid the fluctuation in temperature as well as allowing the TGA to reach equilibrium in terms of reaction gas atmosphere. The reactivity of chars was obtained from the Arrhenius plots of $\ln k$ vs. T^{-1} as shown in Figure 13. Higher regression coefficients ($R^2 > 0.95$) for all the plots confirm that the reaction was in the kinetic controlled regime. The kinetic parameters and the correlation coefficient were determined and are listed in Table 7. To further confirm that the reaction was in the kinetic-controlled regime, an internal effectiveness factor was calculated from Thiele modulus assuming all particles are cenosphical in shape with a wall thickness of 5 μm . The Thiele modulus for cenosphical char as reported by Hodge et al. [5] was used in the calculations. The wall thickness of 5 μm was assumed due to higher swelling ratio. The calculations showed that the effectiveness factor is 1 confirming that the reaction was in the kinetic controlled regime for all the chars below 900 °C (effectiveness factor lower than 1 is an indication of

mass transfer limitation and the kinetics are not true intrinsic kinetics). The variation of effectiveness factor with temperature at 6.2 bar is shown in Figure 14.

The activation energy and pre-exponential factor, shown in Table 7, are independent of the pyrolysis gas atmosphere. Similarly, the pre-exponential factor normalized with surface area also was not significantly affected by the pyrolysis atmospheres. These similarities could have been the result of tar and soot covering the char surface. To confirm the hypothesis, the chars were washed with THF and the kinetic parameters were obtained again. Interestingly, the activation energy and the pre-exponential factor remained unaffected with pyrolysis atmosphere. All these point to pyrolysis gas atmosphere not affecting the activation energy. It is important to emphasize that the reactivity measured here is not just the reactivity of char. In the absence of clear evidence on the concentration of soot before and after THF washing and at 10% conversion, it is safe to say that the kinetic parameters represent the reactivity of not just char but also soot.

Table 7. Kinetic parameters for the chars generated in various pyrolysis atmospheres (at 10% conversion).

Pyrolysis Atmosphere	CO ₂ /N ₂		N ₂		Ar	
	Before THF	After THF	Before THF	After THF	Before THF	After THF
E _a (kJ/mol)	231	205	225	216	230	212
A (s ⁻¹)	6.3 × 10 ⁶	0.4 × 10 ⁶	4.3 × 10 ⁶	1.4 × 10 ⁶	6.2 × 10 ⁶	1 × 10 ⁶
A ₀ (s ⁻¹ bar ⁻ⁿ)	2.8 × 10 ⁶	0.13 × 10 ⁶	2.6 × 10 ⁶	0.6 × 10 ⁶	3.9 × 10 ⁶	0.4 × 10 ⁶
n	0.46	0.65	0.25	0.55	0.29	0.53
A _{int} (gm ⁻² s ⁻¹)	40 × 10 ³	3 × 10 ³	40 × 10 ³	13.7 × 10 ³	60 × 10 ³	ND
SA _{10% conv} (m ² /g)	155	152	113	102	104	ND
R ²	0.973	1.000	0.996	0.999	1.000	0.991

* Error bar with 95% confidence interval around activation energy and pre-exponential factor are ±8.7 kJ/mol and 5.9 × 10⁶ s⁻¹; R²: Regression coefficient; ND: not determined.

Figure 12. Cont.

Figure 12. Instantaneous reaction rates of chars with conversion (before and after washing with THF).

Figure 13. Cont.

Figure 13. Arrhenius plots for chars generated in different gaseous atmospheres.

Figure 14. Effectiveness factor for char- CO_2 reaction at 6.2 bar.

3.3.2. Order of Reaction

The order of reaction was calculated by varying the CO₂ concentration from 25% (1.55 bar) to 100% (6.2 bar). The order of reaction follows the trend: CO₂/N₂ char > Ar char ≈ N₂ char (shown in Table 7). The order of reaction is an indication of the influence of the reactant gas concentration on apparent reactivity [27]. The significance of the order of reaction can be understood from the char-CO₂ reaction mechanism. One of the widely accepted mechanisms postulated by Ergun [28] for char-CO₂ reaction is shown as follows [29,30].

According to the mechanism, the overall rate of the reaction is proportional to the number of carbon–oxygen active complexes formed and desorbed during the reaction. At lower CO₂ partial pressure, not all active sites would form carbon–oxygen complexes. With increase in partial pressure, more active sites form carbon–oxygen complexes. The extent to which the carbon–oxygen complexes form determines the order of reaction. Higher order of reaction for the char pyrolyzed in CO₂/N₂ implies that higher increase in the rate of formation and desorption of carbon–oxygen complexes as the partial pressure was increased from 1.55 bar to 6.2 bar CO₂ pressure. In other words, the reaction rate of the char is highly sensitive to CO₂ concentration. For the chars generated in inert atmospheres (i.e., N₂ and Ar), lower order of reaction can be linked to lower surface area and possibly due to residual products of tar components. The hypothesis that the tar components or the products of tar components contribute to increased reactivity is further confirmed by the significant increase in order of reaction for the THF washed chars. The order of reaction increased considerably by 120%, 83%, and 41% for the chars pyrolyzed in N₂, CO₂/N₂, and Ar, respectively. The correlation between order of the reaction and increase in surface area between the initial char and the 10% char confirms that the order of reaction is a function of surface area.

4. Conclusions

Pyrolysis of a bituminous coal was studied in N₂ and CO₂/N₂ and Ar-based atmospheres in a high pressure, high temperature flow reactor. Chars were obtained at 1100 °C and 6.2 bar with a sampling residence time of ~2.3 s. The volatile yield was highest for the char generated in the CO₂/N₂ atmosphere compared to inert atmospheres, while there was no noticeable difference in volatile yield observed between N₂- and Ar-based environments. The difference in volatile yield with pyrolysis atmosphere was found to be due to gasification of tar and soot by CO₂. Except for the volatile yield, there were no significant differences in the N₂-BET surface areas, lattice parameters of the crystallite carbon, swelling ratio, and the defects to graphite band ratio with pyrolysis atmospheres. The lack of differences with swelling ratio can be attributed to tar/soot deposition. The tar/soot present on the char surface contributed to increased reactivity. The intrinsic reactivity was found to be highest for the char generated in N₂ atmosphere and lowest for the char generated in CO₂/N₂ atmosphere. Both Raman and XRD techniques did not adequately describe the structural differences. The kinetic parameters of the chars were obtained using nth order model. The activation energies were found to be independent of the pyrolysis atmospheres. The order of reaction correlated well with the N₂ surface area.

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