

# Influence of Pressure on Coal Pyrolysis and Char Gasification

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Coal char structure varied greatly with pyrolysis pressure, which has a significant influence on the gasification reactivity. In this study, the influence of pressure on the behavior of coal pyrolysis and physicochemical structure and gasification characteristics of the resultant coal char was investigated using a pressurized thermogravimetric analyzer combined with an ambient thermogravimetric analyzer. First, the pyrolysis of Shenfu (SF) bituminous coal was performed in a pressurized thermogravimetric analyzer (TGA) at different pressures (0.1, 0.8, 1.5, 3, and 5 MPa). The volatile mainly evolved out at 400–800 °C. The gas products are mainly CO<sub>2</sub>, CO, CH<sub>4</sub>, and light aliphatics with some water. It was observed that the pyrolysis of coal was shifted to lower temperature (50 °C) with pressure increasing from ambient to 5 MPa, and the devolatilization rate of coal pyrolysis was decreased and the coal char yield was increased slightly. The structure of solid coal char was analyzed using FTIR, ASAP2020, and CNHS. In the solid char, the main organic functional groups are mainly C=O, C–C (alkane), C–H ar, C–O–C, and C=C ar. The carbon content was increased while H content decreased. Finally, the gasification of the solid char was performed at ambient pressure with CO<sub>2</sub> as gasify agent. The gasification process of coal char can be divided into postpyrolysis and char gasification. Higher pressure accelerated the initial stage of char gasification, and higher gasification reactivity was observed for char derived at 5 MPa.

## 1. Introduction

Pressurized coal gasification is not only the key part of the integrated gasification combined cycle (IGCC) but also the better approach to increase the gasification reaction rate and capacity of gasifier unit. Coal gasification is generally a complex thermochemical process, which consists of pyrolysis (release of volatile) and conversion of residue char (char gasification). Pyrolysis is the initial stage in any gasification process; the treatment condition in pyrolysis strongly affects the yield and the reactivity of the char and consequently influences the subsequent gasification process.<sup>1–4</sup> There have been wide research interests in the effect of pressure on char structure. It was known that the coal char structure varied with pyrolysis pressure, which could cause great changes on the gasification reactivity.<sup>5–9</sup> Wall et al. revealed that the pressure showed a critical impact on coal swelling during the devolatilization. Meanwhile, the reactivity of char particles was changed at high

pressures, and the pressure significantly influences the ash formation through its effect on the structure of chars.<sup>5</sup> Wu et al. found that a highly porous foam char structure tended to evolve during pyrolysis when the pressure increased in a PDTF.<sup>10</sup> Liu et al.<sup>2</sup> observed a similar result that high pressure was favorable for the formation of coal char with high porosity and nonuniform porous structure. It was an advantage for the gasification reaction happened on coal char surface and the diffusion of internal gas phase; hence, the gasification reactivity of the resultant char was increased.<sup>11,12</sup> A measurement by Wu et al. on chars collected from a PDTF showed that both the porosity and the sphericity of a char increased with increasing the pressure up to 1.5 MPa.<sup>6</sup> However, Lee et al. observed that the swelling of coal char was suppressed with pyrolysis pressure increasing, and the surface area was decreased greatly as pressure is higher than 0.8 MPa.<sup>13</sup> Gadiou et al. found that higher pressure extended the residence time of volatile product in the solid particle interior and enhanced the secondary cracking of volatile, resulting in the graphitization degree and the aromaticity increasing greatly, and hence the reactivity of char gasification decreased.<sup>14</sup>

Effects of pyrolysis pressure on char reactivity remain a poorly understood aspect of the coal gasification process. Furthermore, the variation of the chemical structures of coal char particles at different working pressures has rarely been reported. In this study, the influence of pyrolysis pressure on coal pyrolysis and gasification reactivity was performed using

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**Table 1. Proximate and Ultimate Analyses of Coal Sample<sup>a</sup>**

	proximate analysis (wt %, ad)				ultimate analysis (wt %, ad)				
	M	V	A	FC	C	H	N	S	O
SF	10.19	31.62	5.84	52.35	68.84	5.06	0.91	0.28	8.88

<sup>a</sup>M = moisture content, V = volatile matter, A = ash content, and FC = fixed carbon. O content was calculated by difference; ad = on air dried basis.

a pressurized thermogravimetric analyzer. Simultaneously, the physical structure and chemical characteristics of solid coal char resulting from coal pyrolysis were analyzed using FTIR, ASAP2020, SEM, CNHS, etc., analysis instruments. The information observed would be favorable for the development of pressurized coal gasification technology.

## 2. Materials and Method

**2.1. Materials.** The coal sample used is a typical Chinese bituminous coal—Shenfu coal (SF). The original sample was ground and sieved with 100 mesh screen; i.e., the samples analyzed are less than 100 mesh. The result of the proximate and ultimate analysis of coal sample is listed in Table 1.

**2.2. Experimental Methods.** *2.2.1. Pyrolysis of Coal Sample.* The pyrolysis of coal sample was carried out using a pressurized thermogravimetric analyzer (PTGA, Thermal Max 500, Thermal Cahn) with large loading capacity (~100 g) at variant pressure; the sensitivity is 0.01  $\mu\text{g}$ . The repeatability was analyzed with performing a trial twice. It was found that reproducibility was very high, i.e., ~98%, with regard to the limited space; the analysis process was not shown.

To choose a reasonable total flow rate of  $\text{N}_2$  and sample mass, two pre-experiments were conducted: (i) experiments varying sample mass (20–1000 mg) at a fixed  $\text{N}_2$  flow rate (100 mL/min) and (ii) experiments varying the  $\text{N}_2$  flow rate (100–1000 mL/min) at a fixed mass sample (1000 mg). The trial was performed at ambient pressure. The detailed results are not presented here because of space limitations. Hereafter, a brief description is given. Varying the initial sample mass at the range of 100–1000 mg has no significant influence on coal pyrolysis at a flow rate of 100 mL/min. Although when sample size was even smaller (20 mg), pyrolysis of coal was shifted to higher temperatures, which indicates that mass and heat transfer inside the sample particles are negligible with a sample mass that changes from 100 to 1000 mg. A mass of 1000 mg (a large size) was thus chosen in this study to highlight the influence of pyrolysis pressure on the physicochemical structure and gasification characteristics of the resultant solid charcoal. Moreover, varying the flow rate of  $\text{N}_2$  from 100 to 1000 mL/min did not have a significant influence on coal pyrolysis (at a sample mass of 1000 mg), indicating that a flow rate of >100 mL/min is large enough to mitigate the potential difference caused by external heat and mass transfer in the gas phase.

The experimental procedure was briefly elaborated as follows. Sample particles (~1 g) was put in a furnace and held by a quartz crucible previously, and the system pressure was elevated to selected values (0.1, 0.8, 1.5, 3, and 5 MPa) slowly prior to the start of temperature program. After that, the flow rate of the carrier gas was kept at 100 mL/min constantly through the trial in order to mitigate the variance of balance caused by gas flow and abate the noise of mass vs time (temperature) curve. The furnace was then heated up to 1000 °C from the ambient temperature at 10 °C/min and kept for 10 min to complete the pyrolysis. After completing a trial, the furnace was cooled first in order to avoid the volatile evolving for coal char derived at higher pressure; then the back-pressure regulator was released and pressure was changed to atmosphere, and solid coal char residue was collected for further analysis. For pressurized trials, the gas products were exhausted out intermittently controlled by back-pressure regulator to keep the operating pressure constant. Prior to each measurement, the instrument was run to establish the background, for which empty sample pan at selected pressure was taken as the reference, and

the background was automatically subtracted from the pyrolysis curves of coal sample.

As coal was heated, the gas products released out of the TGA were analyzed quantitatively using a portable Fourier transform infrared spectrometer (pFTIR, Temet Gasmet DX-400, Finland) coupled with a hydargyrum cadmium zinc detector (MCTD) and Calmet working station. The transfer line and gas cell were heated to an internal temperature of 180 °C, to avoid condensation or adsorption of semivolatiles products. Each IR spectrum was obtained in 20 s, and the IR scanning range was from 4000 to 500  $\text{cm}^{-1}$ .

*2.2.2. Identification of Solid Coal Char.* The physicochemical characteristics of solid coal char could vary with pyrolysis pressure.<sup>7</sup> The surface structure and chemical compounds of coal chars collected at different operating pressures were identified with the following different approaches.

Fourier transform infrared spectroscopy (FTIR) is a powerful analytical tool for characterizing and identifying chemical bonds.<sup>15,16</sup> The main organic functional group in the char particles observed from coal pyrolysis was analyzed using FTIR (Bruker, Equinox55, Germany) with a DTGS detector. Coal char particles were ground and mixed with KBr powders to prepare the KBr pellets for FTIR analysis. The total weight of pellet was 200 mg, and the amount of coal char sample covered ~1 wt %. The mixture of coal char and KBr powder was dried in an oven at 105 °C overnight. The pellets for FTIR were made under exactly the same conditions, including the sample weight, diameter of pellet, pelleting time, and pelleting pressure. The parameters settings of FTIR were as follows: resolution 4  $\text{cm}^{-1}$ , sensitivity 1, speed 2.5 kHz, filter 1.2, UDR 2, scans to co-add 32, aperture source open fully. Prior to each measurement, the instrument was run to establish the background, for which KBr was taken as the reference. The background was then automatically subtracted from the sample spectrum.

The surface property (surface area, pore distribution, and volume) of solid coal char was examined using an accelerated surface area porosimetry (ASAP 2020) instrument. It was detected using liquid  $\text{N}_2$ , and the isothermal adsorption temperature was set at -196 °C. Moreover, the main organic components (C, H, O, N, and S) of the solid charcoal were analyzed using an elemental analyzer (Vario EL II CNHS/O, Germany). Scanning electron microscopy (SEM, Model Quanta 200, FEI, Dutch) was also used to understand the pore properties of solid charcoal generated from biomass pyrolysis.

*2.2.3. Gasification of Solid Char.* The gasification reactivity of char samples generated in the pyrolysis reactors was measured at atmospheric pressure. The atmospheric reactivity measurements were conducted on both high pressure and atmospheric chars, as such atmospheric measurements provide a common base for investigating the effect of pyrolysis pressure.

Isothermal char gasification experiments were performed with an ambient thermobalance (STA 409C, Netsch Germany) in carbon dioxide at 1000 °C. About 20 mg of charcoal obtained after the pyrolysis was charged into alundum container, which was then placed on the thermal balance (sensitivity is 0.1  $\mu\text{g}$ ). As soon as the sample was heated to 1000 °C at 50 °C/min in a flow of high-purity Ar (100 mL/min), the flow of Ar was switched to pure carbon dioxide (100 mL/min) to start char gasification and maintained for 60 min to make sure the gasification of chars completed. Calculation of char reactivity is based on the following equation:<sup>17</sup>

$$R_T = - \frac{1}{W_0} \frac{dw}{dt} \quad (1)$$

where  $R_T$  is the maximum reactivity (mg/(h mg)) at a temperature  $T$  (°C),  $W_0$  is the initial mass of the char on an ash-free basis (mg),  $dw/dt$  is the maximum value of mass loss rate of char gasification (mg/h), and  $t$  is gasification time (the time on which  $\text{CO}_2$  starts to

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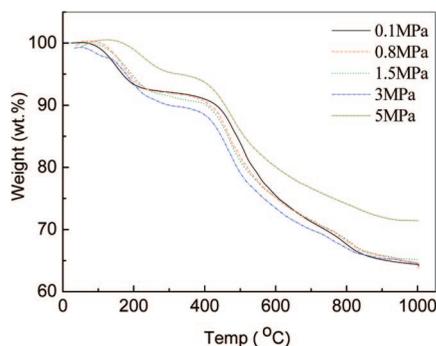


Figure 1. TG curves of SF coal pyrolysis under different pressures.

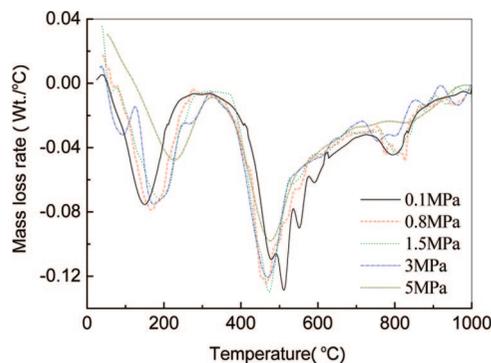


Figure 2. DTG curves of SF coal pyrolysis under different pressures.

input is taken as the initial point of coal char gasification). The larger  $R_T$  means the higher gasification reactivity of the charcoal, which is an efficient index to describe the whole property of char gasification in the comparison at variant condition. Here, it was used to display the gasification reactivity of solid charcoal observed from coal pyrolysis under different pressures.

### 3. Results and Discussion

**3.1. Influence of Pyrolysis Pressure on Coal Pyrolysis.** The TG and DTG curves of SF coal pyrolysis at different pressures are plotted in Figures 1 and 2. The TG curves of empty cubical at selected pressure (not shown here due to the space limit) indicated that the mass was increased with system pressure increasing at the initial stage ( $<100$  °C), especially for pressure at 3 and 5 MPa. It might be attributed to the buoyancy of the quartz crucible caused by the gas flow at high pressures.

From Figures 1 and 2, it can be observed that the pyrolysis of coal samples was taken place at 400–800 °C. As temperature is lower than 400 °C, it is mainly the drying process of coal sample, and moisture removing made a vital contribution to the weight loss. Peaks in DTG curves located at  $\sim 200$  °C corresponded to it. When temperature is higher than 400 °C, the weak bond in the original coal sample commenced breaking, and formed gas product evolved out; they are mainly aliphatics (mainly methane,  $\text{CH}_4$ ) and water (refer to Figure 3). With temperature increasing further, the organic functional groups were broken and reunited quickly, and a big peak was shown in the DTG curve. It might be taken as the primary pyrolysis of coal particles. As displayed in the DTG curves, the peaks of mass loss rate ranged at 400–700 °C. In this stage, the main gas products contained  $\text{CO}_2$ , CO, light aliphatics,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ , etc., as evidenced by FTIR measurements (refer to Figure 3, the typical IR spectra of gas product from SF coal pyrolysis, taken at 560 °C and 0.1 MPa). After that, with temperatures increased further ( $>700$  °C), another weight lost peak was displayed ( $\sim 800$  °C), which might be attributed to the secondary

pyrolysis of condensed carbon matrix, with the evolution of CO. (As space was limited, the IR spectra of gas product from variant temperatures are not shown here.) It is consistent with a previous report; however, during the secondary pyrolysis stage, there was also a large amount of  $\text{H}_2$  releasing out with  $\text{CO}$ .<sup>5</sup>

With pressure increasing from 0.1 to 0.8 MPa and even further, the peak of primary pyrolysis (centered at  $\sim 500$  °C) was shifted to lower temperature. It might be attributed to that higher pressure enhanced the swelling of coal particle prior to the thermal decomposition, and the pore structure of coal particle was upgraded. It is favorable for the breaking of organic functional groups, but higher pressure suppressed the releasing of volatile gas product; the peak value decreased as a consequence. With temperature increased further ( $\sim 800$  °C), the peak value of the secondary decomposition was enhanced with pressure increasing from ambient to 0.8 MPa, as higher pressure extended the residence time of volatile product, which would promote the tar cracking and lead to more light gas products releasing ( $\text{CO}$ ,  $\text{CO}_2$ , etc.). But after that, with temperature increasing further, the peak value was decreased greatly. It showed a similar trend with the primary pyrolysis; the system pressure might be too high, and the suppression to gas product might be larger than the promoting of volatile product caused by higher pressure. The mechanism will be studied in detail soon.

From the TG curve, it can be observed that the total volatile yield decreased and the solid coal char yield increased with increasing pressure, especially for pressure increasing from 3 to 5 MPa. However, in this study, the yield of liquid oil (tar), although it was partly deposited inside the outlet tubing of the TGA, was not considered separately due to the smallness of the sample. With the current equipment, it proved almost impossible to collect and quantify the tar formed. Therefore, the yield of volatile actually includes both gas and oil. The yield of volatile decreased greatly with pressure, whereas the yield of char increased sharply. This is consistent with previous observations.<sup>5,18</sup> Combined the experiment results with the literature,<sup>5,18</sup> it can be deduced that the gas yield increased while tar yield decreased with pressure increasing, as higher pressure enhanced the cracking of tar with more light gas evolving out.

**3.2. Kinetics Calculation of Coal Pyrolysis.** Knowledge of the coal devolatilization rate is of great importance as it exerted a marked effect on the overall gasification behavior.<sup>19</sup> Operating conditions displayed a significant influence on coal pyrolysis behavior; the mechanism was varied with operating pressure, heating rate, and final temperature but also coal type.<sup>20,21</sup> The study on kinetics of coal pyrolysis is necessary to achieve an efficient production of fuel gases, chemicals, and energy. It is also of utmost importance for the proper design of large-scale pyrolysis reactors.

The kinetic parameters of coal pyrolysis under different pressures were calculated on the basis of previous literature.<sup>22</sup> The kinetic parameters of SF coal pyrolysis at different pressures and in the temperature range of 400–1000 °C were calculated. According to the best-fit criteria, the pyrolysis was divided into three stages to analysis the kinetics. The overall activation energy was calculated through weight mean activation energy

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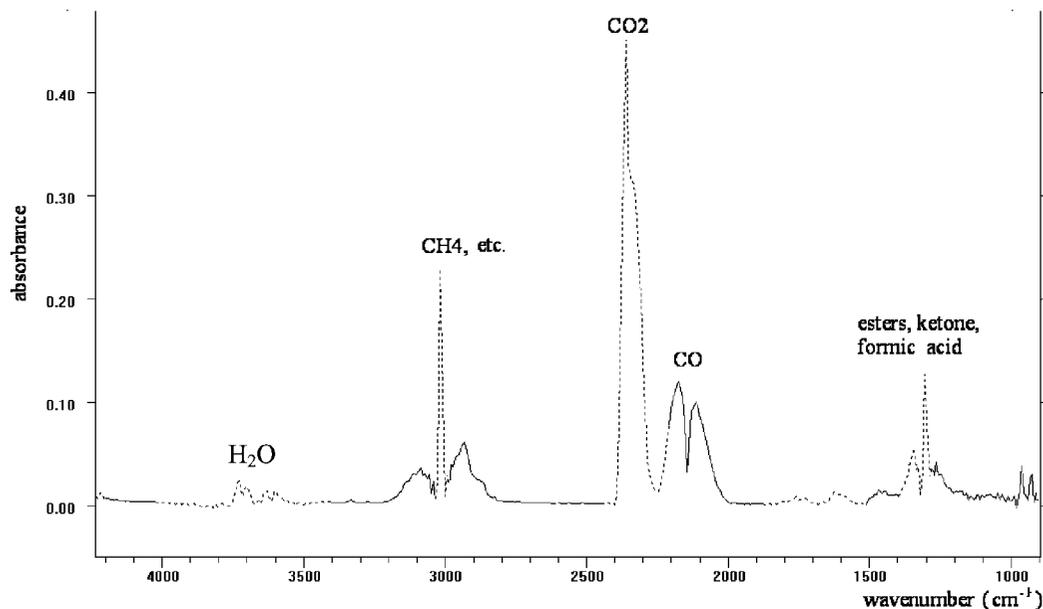


Figure 3. Typical IR spectra of the gas product from coal pyrolysis.

Table 2. Kinetics Parameters of Coal Pyrolysis under Different Pressures

pressure (MPa)	temp (°C)	$n$	$E$ (kJ/mol)	$A$ (s <sup>-1</sup> )	CR <sup>a</sup>	mass loss (wt %)	$E_m$ (kJ/mol)
0.1	430–540	2	44.15	$7.06 \times 10^1$	0.9927	10.12	54.37
	540–760	2	30.82	$7.25 \times 10^0$	0.9989	10.70	
	760–1000	2	126.62	$1.84 \times 10^6$	0.9958	4.92	
0.8	430–535	2	45.77	$1.08 \times 10^2$	0.9981	10.18	44.83
	535–760	2	24.86	$2.54 \times 10^0$	0.9989	9.06	
	760–1000	2	79.23	$4.50 \times 10^3$	0.9962	4.98	
1.5	400–510	2	49.6	$2.17 \times 10^2$	0.9929	10.03	50.12
	510–766	2	27.73	$4.37 \times 10^0$	0.999	10.40	
	766–872	2	122.45	$1.03 \times 10^6$	0.9947	3.29	
3	390–540	2	62.64	$1.88 \times 10^3$	0.9973	11.71	60.22
	540–740	2	33.94	$1.30 \times 10^1$	0.9993	7.29	
	740–850	2	118.28	$9.26 \times 10^5$	0.9903	2.81	
5	400–520	2	67.78	$4.00 \times 10^3$	0.9970	8.80	64.70
	520–780	2	35.86	$1.67 \times 10^1$	0.9993	8.93	
	780–900	2	170.36	$3.98 \times 10^8$	0.9655	2.18	

<sup>a</sup> CR = the correlation coefficient.

( $E_m$ ).<sup>23</sup> The results are listed in Table 2. From Table 2, it can be found that  $E$  of lower temperature increased straightly with pressure increasing from ambient to 5 MPa. It might be attributed to that higher pressure suppressed the volatile removing of coal at low temperature. It is consistent with the result derived from TG and DTG curves (refer to Figures 1 and 2). However, that of middle temperature and high temperature showed a different tendency. First, it decreased greatly as pressure increased from ambient to 0.8 MPa. After that, with pressure increasing further, it increased greatly. It indicated that lower pressure (<0.8 MPa) was favorable for volatile releasing and secondary pyrolysis, while with pressure is higher than 0.8 MPa, and the secondary pyrolysis is much more difficult to undergo.

The total mass loss (the sum of mass loss of three temperature ranges, refer to Table 2) decreased straightly from 25.74% to 19.91% with pressure increasing from ambient to 5 MPa, which confirmed the result that coal char yield increased with system pressure elevating. However, the influence of pressure on coal pyrolysis is very complex. It is believed that pressure affected

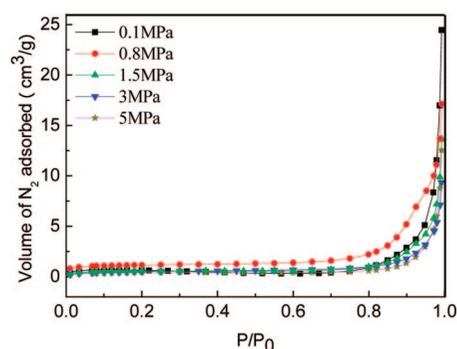


Figure 4. Adsorption curve of coal char from coal pyrolysis under different pressures.

Table 3. Specific Surface Area of Coal Chars from Coal Pyrolysis under Different Pressures

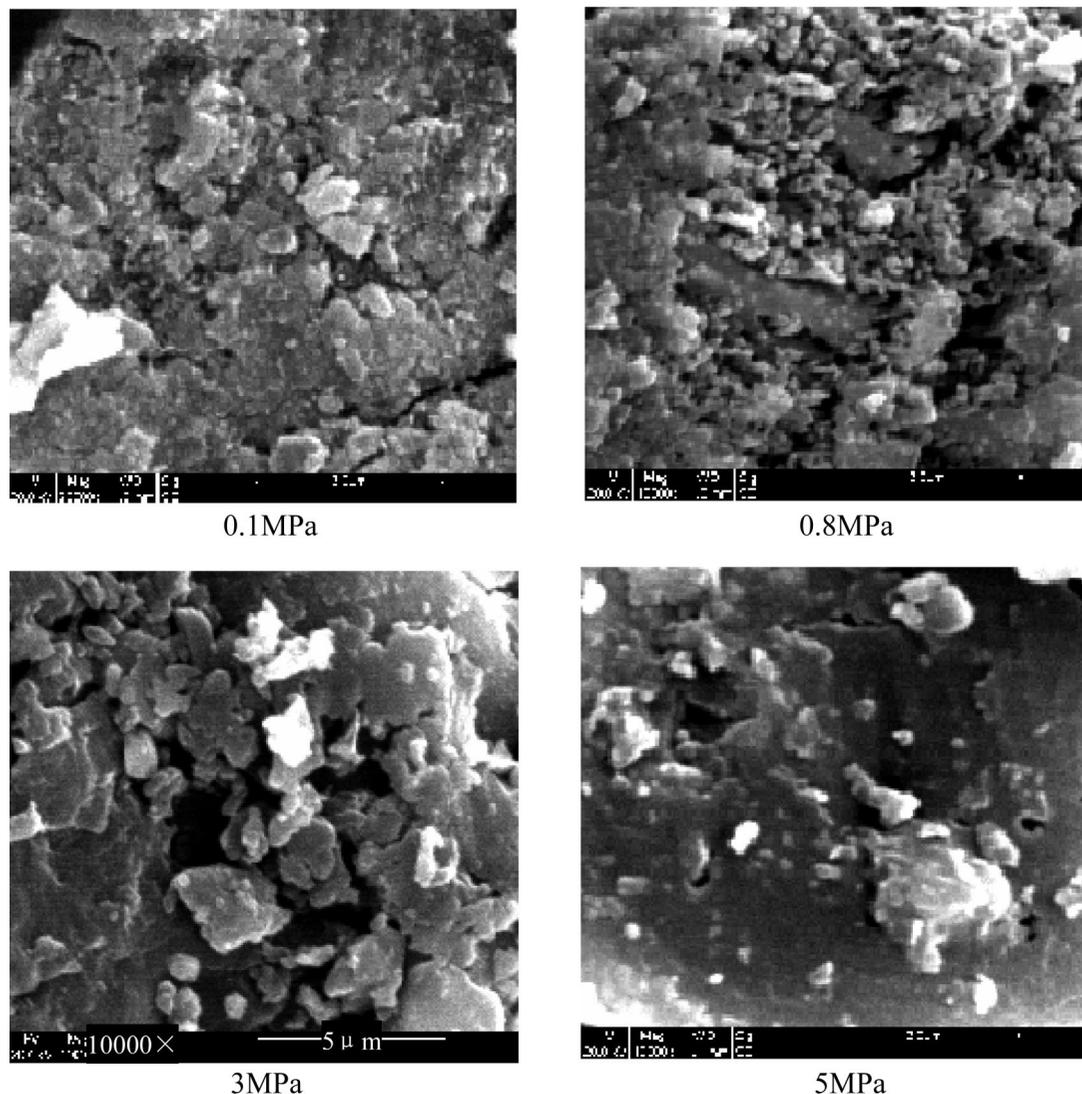
pressure (MPa)	0.1	0.8	1.5	3	5
$S_{BET}$ (m <sup>2</sup> /g)	0.79	3.98	2.00	1.87	1.51
$d_m$ (Å)	250.6	155.4	179.3	149.7	194.2

not only the devolatilization process but also the swelling rate of solid residue.<sup>13</sup>

**3.3. Influence of Pressure on Physicochemical Property of Coal Char.** The physical structure of the resultant coal char was analyzed using ASAP2020. The isothermal adsorption curves are plotted in Figure 4. It can be observed that the adsorption volume increased with relative adsorption pressure ( $P/P_0$ ) increasing, where  $P$  and  $P_0$  are the adsorption pressure of  $N_2$  and ambient pressure (1 atm, ~0.1 MPa), respectively. A greater difference of the adsorption volumes was appeared with pyrolysis pressure variation at  $P/P_0 > 0.8$ . More specifically, when pyrolysis pressure increased from 0.1 to 0.8 MPa, the adsorption volume increased; however, after that, it decreased straightly. It implied that the coal char obtained at 0.8 MPa might have the largest adsorption capacity.

The BET surface area and average pore diameter of coal chars are listed in Table 3. It can be observed that the specific surface area of coal chars increased with pressure and got the maximum value at a pyrolysis pressure of 0.8 MPa. After that, with pressure increasing further, the specific surface area decreased. The average pore size ( $d_m$ ) performed in reverse. It is consistent with Figure 4. It can be concluded that the medium pyrolysis

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**Figure 5.** SEM picture of coal char from coal pyrolysis under different pressures.

pressure (0.8 MPa) is favorable for solid charcoal to get higher BET surface areas with a large amount of fine pores, to hopefully accelerate the gasification process of coal.

The SEM picture (Figure 5) displayed results similar to those found with  $S_{\text{BET}}$  in Table 3. As the space is limited, only the SEM photos of solid charcoals at 0.1, 0.8, 3, and 5 MPa are shown. The picture was taken at 20 kV with magnificent time at  $\times 10000$ . From the photo, it can be observed that the surface of solid char obtained at ambient pressure is quite smooth with countable large pores. As pyrolysis pressure increased to 0.8 MPa, the surface of char particles became coarse, and the pore number increased greatly, and the surface structure of solid coal char was enriched. After that, with pressure increasing further, fine pores diminished while a few large pores formed, which testified the result observed from Table 3 that  $S_{\text{BET}}$  decreased while the average pore diameter increased greatly. The following reason might contribute to it: higher pressure ( $>0.8$  MPa) suppressed the swelling of coal particles, and it blocked the releasing and cracking of volatile (organics components), which covered the surface and closed the fine pores.

With pressure variant, chemical structure displayed great change as well as the surface structure.<sup>14</sup> The main elemental component of the solid coal char residue was analyzed, listed in Table 4. It can be observed that the C content increased while H content decreased slightly with pressure increasing. It confirmed the previous result that higher pressure is favorable

**Table 4.** Ultimate Analysis of Solid Coal Chars

<i>P</i> (MPa)	C (wt %)	H (wt %)	N (wt %)	S (wt %)
0.1	79.71	0.48	0.71	0.53
0.8	80.59	0.38	0.72	0.59
1.5	80.60	0.37	0.73	0.59
3	81.46	0.36	0.75	0.57
5	82.04	0.34	0.73	0.59

for the secondary pyrolysis of volatiles, and more H-bearing gas products were formed and released.

The IR spectra of the solid coal char observed from trials under different pressures are plotted in Figure 6. As no obvious IR absorbance was displayed in the range of 4000–2000  $\text{cm}^{-1}$ , only the IR spectra at 2000–400  $\text{cm}^{-1}$  are shown. The compounds contained in coal char were mainly carbonyl (C=O, 1723  $\text{cm}^{-1}$ ), benzene stretch ring (C=C, 1587  $\text{cm}^{-1}$ ), C–O–C (1345  $\text{cm}^{-1}$ ), aromatic hydrogen (C–H, 835  $\text{cm}^{-1}$ ) with some C–C stretching (708  $\text{cm}^{-1}$ ), etc. It can be observed that the IR absorbance of CH ar., C–C al., and C–O–C decreased greatly as the pyrolysis pressure increased from the ambient to 5 MPa, and that of C=O (1723  $\text{cm}^{-1}$ ) and C=C ar. (1587  $\text{cm}^{-1}$ ) decreased gently. It indicated that these organic functional groups diminished with the cracking of aromatic and alkanes components during coal pyrolysis under higher pressure. So the organics compound residue in the solid coal char were reduced greatly as the secondary cracking was enhanced with system

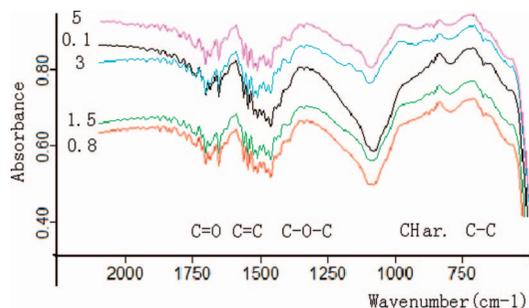


Figure 6. IR spectra of coal char from SF coal pyrolysis at different pressures.

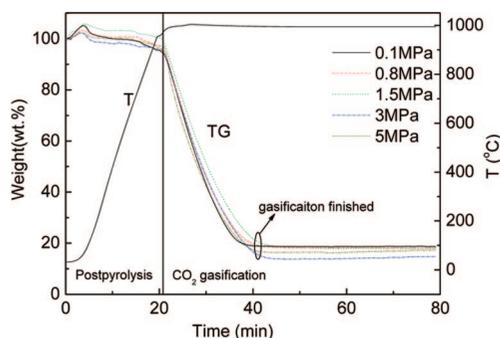


Figure 7. TG curves of solid coal char gasification.

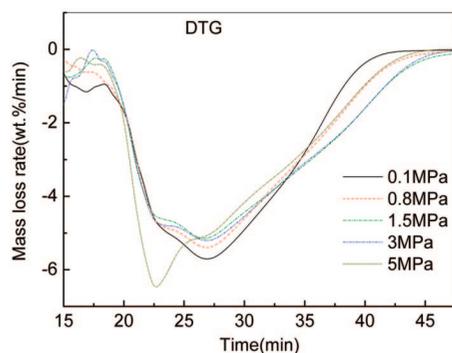


Figure 8. DTG curves of solid coal char gasification.

pressure increasing. From Table 4 and Figure 6, it was derived that the graphitization of the solid charcoal might increase with pyrolysis pressure increasing. It is unfavorable for the gasification of charcoal.

**3.4. Influence of Pyrolysis Pressure on Char Gasification Reactivity.** The pressure at which the parent coal is devolatilized also plays an important role in the reactivity of the resulting char. The gasification profiles of solid char obtained from SF pyrolysis at different pressure are plotted in Figures 7 and 8 in TG (wt %) as well as DTG (wt %/min). As temperature was lower than 1000 °C, which was the postpyrolysis stage, there is just some external moisture or volatile residue removing. As the time period of postpyrolysis is very short, the weight loss is not obvious. Once temperature reached 1000 °C, Ar was switched to CO<sub>2</sub>, and the gasification of solid char started. With retention time extending, solid charcoal reacted with CO<sub>2</sub> quickly. From the gasification curves, it can be observed that the gasification reaction was completed in 25 min (from 20 to 45 min; refer to Figures 7 and 8) with some ash residue, and

Table 5. Gasification Reactivity of Solid Coal Chars (1000 °C)

pressure (MPa)	0.1	0.8	1.5	3	5
$R_T$ (mg/(h mg))	3.75	3.55	3.33	3.38	4.22

after that, no obvious weight loss was detected with time extending further. For the initial stage, the gasification was accelerated with pyrolysis pressure increasing, especially for 5 MPa. It might be attributed to the more volatile residue on solid char surface at higher pressure (refer to Figure 2). After that, the gasification rate was hindered by pyrolysis pressure (23–35 min, refer to Figure 8), and the maximum mass loss rate was decreased greatly, but not for char made at 5 MPa.

The gasification activity of solid char is calculated using eq 1, and the results are listed in Table 5. It can be observed that the gasification reactivity decreased with pressure increasing from ambient to 1.5 MPa. However, after that, it increased greatly and got the maximum value at 5 MPa. It is consistent with the result observed from gasification curves (Figure 8), which might be the combined result of the variant of surface structure coal char formed at different pressure and chemical property as well. The correlation in detail will be studied in the near future.

#### 4. Conclusions

The influences of pressure on coal pyrolysis, physicochemical characteristics, and gasification reactivity of resultant coal chars were investigated systematically. The conclusions can be drawn as follows.

The devolatilization of SF bituminous coal mainly happened at 400–800 °C, the pyrolysis process of SF coal included moisture removing (<400 °C), primary pyrolysis, and secondary pyrolysis. It was shifted to lower temperature with pressure increasing. The decomposition was enhanced as pressure is lower than 1.5 MPa; after that, it was lowered greatly. It was found that second order is most suitable for the pressurized pyrolysis of SF coal particles, and the activation energy observed is the lowest value at 0.8 MPa.

The surface structure and chemical property of solid coal char were varied greatly with pressure increasing. The surface area of coal char increased with pressure increasing when pressure was less than 0.8 MPa; after that, it decreased straightly. The organic compounds on charcoal surface contained mainly C=O (1723 cm<sup>-1</sup>), C=C (1587 cm<sup>-1</sup>), C-O-C (1345 cm<sup>-1</sup>), and C-H ar. (835 cm<sup>-1</sup>) with some C-C stretching (708 cm<sup>-1</sup>). These compounds diminished straightly with pressure increasing. Simultaneously, C content in the solid residue increased while H content decreased with pressure increasing.

The gasification of solid char comprised postpyrolysis and gasification. Higher pressure is favorable for the initial of char gasification, while lowering the maximum loss rate. The gasification reactivity of solid char decreased first with pyrolysis pressure increased from ambient to 1.5 MPa; after that, it increased and got the maximum value at 5 MPa.

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