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Influence and action mechanism of pressure on pyrolysis process of a low rank Naomaohu coal at different temperatures



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Keywords: Pressurized pyrolysis Promoting effect Inhibiting effect Char physicochemical properties Action mechanism

ABSTRACT

In this study, the effect of pressure on the pyrolysis characteristics of Naomaohu coal and the physicochemical properties of char during slow pyrolysis is evaluated, and the mechanism of pressure is explored. The results show that the influences of pressure on char yield and physical properties are reflected in both promoting and inhibiting effect, and the latter is more obvious with the increasing temperature. As the pressure increases, the char yield first reduces and then improves, and at $600 \,^\circ$ C and $800 \,^\circ$ C the minimum yields are in 1.0 MPa and 0.1 MPa, which are 57.48% and 54.04%, respectively. The S_{BET} of char increases first and then decreases. At $800 \,^\circ$ C, the S_{BET} of char increases from 7.86 m²/g at 0.1 MPa to 19.81 m²/g at 0.5 MPa and then decreases. The effect of pressure on the chemical properties of char is relatively simple. As the pressure rises, the content of functional groups in char reduces and the degree of graphitization enhances. The TG-DTG curve, XPS, BET, SEM test, experiments on the pressurized micro-fluidized bed reaction analyzer and pressurized pyrolysis-gas chromatography/mass spectrometry show that the pressure mainly affects the pyrolysis process by affecting the secondary reaction of the primary volatiles in the particle and is related to temperature.

1. Introduction

In the context of carbon neutrality, it is urgent to transform existing thermal power units to achieve clean electricity production [1]. Studies have shown that pressurized pyrolysis can not only reduce the emission of pollutants [2–4], improve the conversion rate of coal in the thermochemical conversion process [5], but also improve the efficiency of the polygeneration system [6]. Therefore, with the development of clean coal technology and the proposal of carbon neutrality goals, the thermochemical conversion process under pressure has attracted more attention [5]. What's more, the reserves of low-rank coal account for more than half of the total coal reserves in China [7]. According to the physical and chemical properties, it can be known that low-rank coal is the most suitable coal for pyrolysis [8]. Hence, it is necessary to explore the influence of pressure on the low-rank coal pyrolysis process to provide a reliable theoretical basis for the parameters design of pressurized equipment.

There are many studies on the influence of pressure on coal pyrolysis characteristics. Temperature is the most important factor affecting pyrolysis process. Sun et.al studied pressurized pyrolysis of coal and found the total weight loss decreased with pressure at high temperatures while

that was almost independent at low temperatures [9]. Zhang et.al conducted coal pressurized pyrolysis at 1000 °C and demonstrated that the BET surface area (SBET) of the char increased [10]. Bai et.al found pressure had little effect on SBET in 700 °C [11], while Lin et.al confirmed that the S_{BET} reached its maximum value at 1 MPa and 800 $^\circ C$ [12]. Some researchers have found that the crystal structure of char became more orderly as pressure increased in the temperature range of 600-900 °C [13]. Zhang et.al conducted a pressurized pyrolysis experiment in the pressurized drop tube furnace. The results showed that the increase of pressure can promote the transformation of the smaller aromatic structure into a larger aromatic structure, and the graphitization degree was more obvious at 1000 °C [14]. But Roberts summarized pressure had no effect on the chemical structure of char at 1100 °C [15]. The conclusions about the effect of pressure on the thermochemical behavior and the physicochemical properties of char are inconsistent, showing that the action mechanism of pressure is largely affected by temperature. It has reported that the influence of pressure on pyrolysis process was related to temperature [9], but no detailed research has been carried out, so it is necessary to supplement research in this area to make the action mechanism of pressure more comprehensive.

The effect of pressure on pyrolysis process is generally inhibition in

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the existing studies, that is, the escape of volatile compounds is suppressed and the secondary reaction is strengthened with the increasing pressure [14,16,17]. Zhang et.al found that the elevated pyrolysis pressure inhibited the escape of volatiles and enhanced the secondary reaction of tar [5]. Yan et.al reported that high H₂ pressure prolonged the residence time of volatiles and aggravated the secondary cracking reaction, resulting in a decrease in tar yield and an increase in CH4 yield [18]. Arash et.al observed that the S_{BET} and swelling ratio of char reached the maximum value at 1 MPa [13], indicating the existence of an optimal pressure point, but the action mechanism of pressure was not explained and verified in detail. However, a few studies suggested that there was more than one mechanism for the effect of pressure on pyrolysis. The escape of volatiles is accelerated at low pressure, but that is inhibited and the secondary reaction is enhanced at high pressure [19]. But the promotion mechanism of pressure has not been studied in more detail, and whether the impact of pressure on the thermochemical process and the physicochemical properties of char is same remains to be verified. Meanwhile, it can be seen from the above that whether these two mechanisms are related to temperature also needs to be verified.

Naomaohu coal is a kind of low-rank coal that has high H/C and volatile content, and low ash [20], which is a suitable coal type for the low-rank coal pyrolysis polygeneration technology. It is necessary to conduct pyrolysis experiments for this particular type of coal to investigate its pyrolysis law under pressure and provide basic experimental data for its industrialization. To examine these issues, this work takes Naomaohu coal as the raw material to study the effect of different final temperatures (600-800 °C) and pressure (0.1-1.5 MPa) on coal pyrolysis characteristics in a pressurized thermogravimetric analyzer (P-TGA), including thermochemical process and physicochemical properties of char. The mechanism of pressure on the physicochemical properties of char is explored through characterization tests. Finally, relevant experiments are carried out on a pressurized micro-fluidized bed reaction analyzer (P-MFBRA) and pressurized pyrolysis-gas chromatography/mass spectrometry (PPY-GC/MS) to verify the action mechanism of pressure.

2. Methods and materials

2.1. Coal samples preparation

The Naomaohu coal from Xinjiang Province of China is ground and sieved to a particle size range of 75–125 μ m. The proximate and ultimate analyses are shown in Table 1.

2.2. Pyrolysis experiments in P-TGA

The pressurized pyrolysis of coal is implemented in a P-TGA (Thermal Max500, Thermo Fisher Scientific Corporation, USA). Three gas streams including purge gas, furnace gas, and reaction gas are introduced into the P-TGA as shown in Fig. 1. Ar is used as purge gas and furnace gas with a flow rate of 0.6 L/min and 0.5 L/min respectively to protect balance components and furnace body.

The increase in gas density under high pressure causes apparent weight gain, so a blank experiment must be conducted to remove the influence of buoyancy. Under each pressure condition, the pyrolysis of the empty sample is completely consistent with the experimental conditions, and then the coal pyrolysis experiment is carried out. Finally, the two sets of data are subtracted according to the same temperature and pressure, and the weight gain caused by gas buoyancy is removed. Fig. 2 shows the TG curve of the blank experiment under different pressures. In addition, in order to eliminate the influence of buoyancy, the sample mass is selected as 100 mg after adjustment. The detailed explanations are added in the supplementary.

The experiment process is as follows. Put ~100 mg sample in a quartz crucible. To avoid large gas disturbance, the gas flow rate is maintained at 0.5 L/min. The system pressure is elevated to the set value, and the backpressure valve is adjusted to balance the inlet and outlet gases in the reactor to ensure that the pressure remains stable during pyrolysis process. After pressure stabilizes, the reactor is heated from room temperature to experimental temperature at a heating rate of 20 $^\circ\text{C}/\text{min}$ and kept at different final temperatures for 10 min to ensure the completion of pyrolysis. Char obtained under different conditions is denoted as $Char_{x-y}$, where x and y represent temperature and pressure. Each experiment is implemented at least three times to ensure the reproducibility and reliability, and $Char_{x-y}$ is mixed and collected for characterization tests. The working conditions are shown in Table 2. The amount of volatiles released is very small at low temperature, in order to obtain sufficient volatile analysis in the industry, the pyrolysis temperature is generally higher. In order to obtain more volatile matter, and to compare the influence of pressure at relatively low temperature and high temperature, three pyrolysis temperatures of 600 °C, 700 °C and 800 °C are selected in this paper.

2.3. Structural characterizations of char

All samples used for characterization tests are mixed samples after repeated experiments. The elemental contents of char, including C and H are determined by means of an elemental analyzer. The pore structure parameters of char are analyzed with an Accelerated Surface Area and Porosimetry System, ASAP 2020. Brunauer-Emmett-Teller (BET) and Brrrett-JovnerHalenda (BJH) are employed to calculate and obtain specific surface area and pore size distribution, respectively. The Fourier transform infrared (FTIR) spectrometer, Thermo Scientific Nicolet iS50, is used to characterize the evolution of functional groups on the char surface. The crystal structure parameters of char are analyzed by X-ray diffraction (XRD), D8 ADVNCE. The XRD are recorded with a stepscanning method in the range of 10-80°. The surface element distribution of char is measured by X-ray photoelectron spectrometer (XPS), ESCALAB 250XI. The original XPS spectrum is fitted by Gaussian and Lorentz functions, and the C1s spectrum (280-294 eV) is fitted into five peaks.

2.4. Pressurized pyrolysis experiments in P-MFBRA and PPY-GC/MS

Due to the structure of P-TGA in this study, it is impossible to collect gas and liquid products for yield and composition analysis. Therefore, P-MFBRA and PPY-GC/MS are used in this work to verify the promoting action mechanism of pressure. The introduction of P-MFBRA and PPY-GC/MS has been covered in detail in those researches [21,22]. In order to verify the mechanism of promoting and inhibiting of pressure, the following experiments are carried out in the P-MFBRA and PPY-GC/MS. The experiments in P-MFBRA are as follows. After the reactor is heated to 600 °C and 800 °C, the samples are placed into the feed container, the backpressure valve is closed, the pressure increases to the experimental pressure, and then the backpressure valve is adjusted to keep the pressure stable. After the pressure and temperature

Table 1

Proximate and ultimate	analyses	of the	Naomaohu	coa

Proximate analysis (wt%)			Ultimate an	Ultimate analysis (wt%, daf)					
M _{ad}	A _{ad}	V_{daf}	FC _{daf}	С	Н	0	Ν	S	H/C molar ratio
2.65	5.31	50.26	49.74	65.93	3.56	29.31	0.80	0.40	0.65



Fig. 1. The schematic diagram of the P-TGA.



Fig. 2. TG curve of empty crucible under different pressures.

Table 2The experiment conditions.

Parameter	Value	
P-TGA		
Temperature(°C)	600, 700, 800	
Pressure(MPa)	0.1, 0.5, 1.0, 1.5	
Gas flow rate(L/min)	0.5	
Heating rate(°C/min)	20	
Holding time(min)	10	
P-MFBRA		
Temperature(°C)	600, 800	
Pressure(MPa)	0.1, 0.5, 1.0	
PPY-GC/MS		
Temperature(°C)	600	
Pressure(MPa)	0.1, 1.0, 1.5, 2.0	

are stabilized, the fluidized medium is in uniform fluidization state, and the sample is rapidly injected into the reactor. The release characteristics of main pyrolysis gases are determined by mass spectrometry online and micro gas chromatography. The experiments in PPY-GC/MS are as follows. The sample cup containing about \sim 0.8 mg coal sample is put

into the reactor, and isothermal pyrolysis reaction is performed at 600 °C under different pressures. The pyrolysis products are detected by gas chromatography/mass spectrometry. Gas products are quantified by external standard method, and each component in tar is quantified by peak area normalization method. The mass of char is calculated by weighing the mass of the sample cup before and after the reaction.

3. Results and discussion

3.1. The influence of pressure on char yield

Deng et.al studied the pressurized pyrolysis process of demineralized coal at 1000 °C and found that as the pyrolysis pressure increased from 0.1 MPa to 1.5 MPa, the char yield increased from 64.81% to 68.78%, which was attributed to the increase of external pressure, the pressure difference between internal and external pores of coal decreased, and the macromolecule tar was remained in the condensed phase, increasing the char yield [23]. In this work, the change of char yield at 800 °C is consistent with Deng, but it is not the same at low temperature.

As shown in Fig. 3, at 600 $^{\circ}$ C, the char yield decreases from 59.37% at 0.1 MPa to 57.48% at 1.0 MPa, while at 800 $^{\circ}$ C, the carbon yield



Fig. 3. Char yield of coal pyrolysis under different pyrolysis conditions.

increases from 54.04% to 56.12% when the pressure increases from 0.1 MPa to 1.5 MPa. There are two effects of pressure on char yield. One is the decrease of char yield under pressurized condition, known as the promoting effect. Due to the high volatile and hydrogen content of Naomaohu coal, at low temperature, tar free radicals and coal char undergo hydrogenation reaction, gas products and tar increase, and the char yield decreases [24-26], increasing the pressure within a certain range promotes this process. Furthermore, pressurization enhances the heat transfer rate of coal char and the movement rate of molecules [27], causing an increase in the release rate of volatiles and a decrease in the probability of secondary reactions of tar. Second is the increase of char yield under pressurized pyrolysis, known as the inhibiting effect. Under high pressure, the escape of volatiles is inhibited, and the tar is more likely to undergo secondary reactions to form deposited carbon [28]. The higher the temperature, the more obvious the inhibiting effect of the pressure. With the increase of pressure, the char yield first decreases and then increases at 600 °C and the inflection point appears at 1.0 MPa, while the char yield keeps increasing at 800 °C. This is because the probability of secondary reactions of tar improves with the rising pressure, resulting in the inhibiting effect of pressure is greater than the promoting effect. The inflection pressure point appears earlier under higher temperature.

3.2. The influence of pressure on the physical structure of char

3.2.1. The effect of pressure on the pore structure of char

The BET surface area, pore volume and average pore width of char_{x-y} are shown in Table 3. Fig. 4 shows the distribution of pore volume with pore size. At 600 °C, the pore volume consists mainly of pores of 0–20 nm and 20–60 nm. As the pressure increases from 0.1 MPa to 1.5 MPa, the contribution of pores of 20–60 nm to the pore volume increases, and the contribution of pores of 0–20 nm to the volume first increases and then decreases. When the temperature is increased to 800 °C, the pore volume of the char mainly consists of pores of 0–20 nm. With increasing pressure, the change in pore volume is mainly associated with pores of 0–20 nm.

The S_{BET} of coal char changes with pyrolysis temperature and pressure are shown in Fig. 5. The effect of pressure on S_{BET} is related to temperature and more complex. The S_{BET} increases first and then decreases with pressure, but the inflection point advances as temperature rises. Previous report also observed the existence of an optimal pressure value but did not further explore the effect of pressure versus S_{BET} at different temperatures [16]. The swelling degree of coal char is positively correlated with the pore structure [29,30]. As pressure increases, the char fluidity and the amount of gas released increases, resulting in an increase in the rate of bubble generation and particle swelling. On the other hand, higher pressure restrains the growth of bubbles and reduces particle swelling [31–33]. The competitive reaction leads to the existence of the optimal pressure, where the swelling rate and S_{BET} is the highest and largest, respectively. As temperature rises, the gas density

Table	3
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Porous structural	l properties	of the	char _{x-y}	sampl	es.
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T (°C)	P (MPa)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)
600	0.1	1.589	0.005183	11.09
	0.5	1.619	0.007374	10.14
	1.0	2.213	0.007463	10.88
	1.5	1.583	0.006054	12.27
700	0.1	3.675	0.008459	6.83
	0.5	4.228	0.010457	7.16
	1.0	7.360	0.015468	5.69
	1.5	4.731	0.010539	7.67
800	0.1	7.864	0.017295	5.77
	0.5	19.98	0.02498	5.18
	1.0	11.31	0.024646	5.84
	1.5	9.372	0.021231	5.70

becomes greater and the maximum value point is advanced. It can be seen from Fig. 5(b) that the pore size distribution of char is mainly macropores and mesopores. The pores gradually change to small mesopores with temperature, but the change of pores with pressure is more complicated, mainly because the deposited carbon produced by the secondary reaction covers the surface of the coal char, making the macropores change to mesopores and resulting in different changes in the pores. In order to further verify the impact of pressure on the char surface, the surface morphology of char_{800-y} at different pressures are analyzed by SEM.

3.2.2. Surface morphology

Fig. 6 shows the surface morphology of $char_{800-y}$ at different pressures by SEM. It can be seen from the Fig. 6 that the surface of the particles is broken under pressure, and there is a violent expansion and the pores increase, especially from atmosphere to 0.5 MPa. The increase of pressure leads to the increase of porosity and the number of bubbles, but too high pressure will suppress the continued expansion of particles [30]. Secondly, the deposited carbon generated by secondary reaction of tar under high pressure covers the surface of char [34], and the higher the pressure, the more obvious it is. Hence, when the pressure increases after 0.5 MPa, there is no obvious change in morphology of char, but the pore structure of char decreases at 1.5 MPa.

3.3. The impact of pressure on the chemical structure of coal char

3.3.1. Evolution of functional groups on the surface of char

FTIR is used to study the evolution of functional groups for char. This work divides the infrared spectrum into four wavenumber regions [35]: (1) 900–680 cm^{-1} , the vibration peaks of aromatic carbon-hydrogen bonds; (2) 950–1350 cm⁻¹, the vibration peaks of carbon-oxygen single bonds; (3) 1400–1800 cm⁻¹, carbon-oxygen double bonds stretching vibrations, aromatic ring carbon-carbon double bonds; (4) $2800-3000 \text{ cm}^{-1}$, the vibration peaks of aliphatic hydrocarbon carbon-hydrogen bonds. To perform semi-quantitative analysis, the FTIR is normalized and the results are shown in Fig. 7. And the effect of temperature on the carboxyl group is greater than that of the pressure [36], so the 1400–1800 cm^{-1} band does not show a monotonous trend with pressure changes. The shape of the peaks changes with the increase of temperature, while the size of the peaks changes with the increase of pressure indicating that the types and the content of functional groups have changed significantly, respectively. With the increase of pressure, the absorption peaks of $2800-3000 \text{ cm}^{-1}$ (C-H) and $950-1350 \text{ cm}^{-1}$ (C-O) on the char surface significantly decrease. This is because aliphatic hydrocarbons and oxygen-containing functional groups with lower bond energy are decomposed, releasing more H₂O, CO₂, and H₂, and the fatty chain is shortened. The effect is more pronounced at high temperatures. The weakening of the stretching vibration at $680-900 \text{ cm}^{-1}$ (C-H) indicates that the relative content of aromatic hydrogen is reduced, meaning that the increase in pressure promotes the secondary reaction of semi coke, strengthens the dehydrogenation and polycondensation of aromatic rings in char, and deepens the degree of graphitization of char.

3.3.2. Evolution of char microcrystalline structure

The XRD pattern of char is shown in Fig. 8. It can be seen that there are two peaks at $\sim 23^{\circ}$ and $\sim 43^{\circ}$, representing the (002) band and the (100) band, respectively. The (002) band and the (100) band indicates the degree of orientation of the aromatic layer in microcrystal and the size of the aromatic layer in microcrystal respectively. These two bands can be used to describe the graphite-like structures (crystalline carbon) of coal char [37,38]. As pressure increases, the fluidity of char in the plastic stage increases, leading to an increase of particle expansion and the graphitization of char in the recirculation stage [39]. Hence, with the increase of pressure and temperature, the (002) band gradually approaches to the direction with better graphitization degree and the peak shape gradually becomes sharp and asymmetric, which means that



Fig. 4. Cumulative pore volume and Pore size distribution curves of char_{x-y} at (a) 600 °C, (b) 700 °C, (c) 800 °C.



Fig. 5. Porous structure of char prepared at different pyrolysis conditions: (a) BET specific surface area, (b) average pore size.



Fig. 6. The SEM of char at 800 °C and different pressures. (a)0.1 MPa, (b)0.5 MPa, (c)1.0 MPa, (d)1.5 MPa.



Fig. 7. FTIR spectra of the char prepared under different pyrolysis pressures: (a) 600 °C, (b) 700 °C, (c) 800 °C.



Fig. 8. XRD spectra of char prepared at different pyrolysis conditions.

the orientation degree of the aromatic layer of the coal char is deepened. The (100) band gradually appears and develops towards a higher direction, indicating that the aromatic nucleus of coal char has a higher degree of condensation. The evolution of the peak shape shows that the graphitization degree of char is deepened.

Study has shown that the peak appearing at $5-35^{\circ}$ is the peak formed by the overlapping of (002) band and (γ)band [40]. The (002) band represents aromatic carbon, whereas (γ) band reflects amorphous

substance. The curve is fitted to explore the influence of pressure on the microcrystalline structure of coal char in more detail. Fig. 9(a) represents the typical fits of two Gaussian peaks for the $\sim 26^{\circ}$ band of char. The microcrystalline structural parameters are calculated according to the Bragg and Scherer equations [13,41]:

$$A_{002} = \frac{\lambda}{2sin\theta_{002}} \tag{1}$$

$$L_c = \frac{0.94\lambda}{\beta_{002} cos\theta_{002}} \tag{2}$$

$$L_a = \frac{1.84\lambda}{\beta_{100}cos\theta_{100}} \tag{3}$$

$$n = \frac{L_c}{d_{002}} \tag{4}$$

where d_{002} is the interplanar distance of aromatic layers of microcrystalline (Å), L_c represents the height of microcrystalline (Å), β is the fullwidth at half maximum, L_a represents the diameter of microcrystalline (Å), n is the maximum number of aromatic layers, λ is incident wavelength ($\lambda = 1.5432$ Å).

Results are shown in Fig. 10. At different temperatures, as the pressure increases from 0.1 MPa to 1.5 MPa, d_{002} decreases slowly and orderly, indicating the degree of graphite-like structures of coal char gradually deepens, but it is all higher than the ideal graphite interlayer spacing (0.3354 nm). The increase of *n* indicates that the number of aromatic layers in the carbon increases with increasing pressure. The increase of L_c and L_a indicates that the microcrystalline structure of coal



Fig. 9. Fitting curves of the (a) XRD and (b) XPS peaks for the char.



Fig. 10. Changes of structural parameters of coal char as a function of pyrolysis pressure under different pyrolysis temperatures. (a) d₀₀₂; (b) Lc; (c) La; (d) n.

char has been simultaneously increased in the crystal lattice and the crystal plane. Pressure has greater influence on d_{002} , L_c and n at 800 °C, indicating that the weight of the influence for pressure on coal char microcrystalline structure increases with temperature. The results of XRD and FTIR prove that the impact of pressure on chemical properties of the char is relatively simple. The pressure increased from 0.1 MPa to 1.5 MPa, which promoted the polycondensation reaction of the semi coke, and the higher the temperature, the stronger the polycondensation reaction of the char under pressurized condition.

3.4. Verification of the action mechanism of pressure on pyrolysis process

3.4.1. Thermochemical behavior of coal under different pressures

The coal pyrolysis can be divided into three stages, drying stage, depolymerization and decomposition stage and polycondensation stage [42]. It can be seen from Fig. 11 that pressure has different influences on coal pyrolysis process at low (600 °C) and high (800 °C) temperatures.

At the drying stage and depolymerization and decomposition stage, the influences of pressure at final temperatures of 600 °C and 800 °C are basically the same. High pressure leads to the shift of the DTG curve to the high temperature zone in first stage. In the second stage, with the



Fig. 11. TG-DTG curves for the pyrolysis of coal under different pyrolysis conditions.

increase of pressure, the position of DTG peak gradually tends from high temperature region at 0.1 MPa to low temperature region at 1.5 MPa, and the escape of volatile matter is accelerated.

Pressure has different effects on pyrolysis process in the polycondensation stage at different final temperatures. The role of pressure is reflected in two aspects. On the one hand, the accumulation of light volatile gases will generate forced flow, which accelerates the escape of volatile gases. On the other hand, pressure will inhibit the escape of volatiles. And those are related to temperature [19]. Therefore, at 600 °C, the former dominates as the pressure increases, while the latter is more obvious at 800 °C.

3.4.2. XPS analysis of the char structure

The original XPS spectrum of char and the distribution law of C and O functional groups on char surface are shown in Fig. 12. According to previous research, there are five fitting peaks of C1s spectrum [14]. Fig. 9(b) shows the results of curve fitting and Table 4 lists the corresponding binding energies of different functional groups. The distribution of different bonds is compared by calculating the relative area of the fitting peaks. It can be seen from Fig. 12(a) that with the increase of pressure, the relative content of C increases, while that of O decreases first and then increases. The C=C/C-C bonds and C-H bonds are the main forms of carbon. With the increase of pressure, the relative content of C=C increases and that of C-H decreases. To further explain the change of H element in char with increasing pressure, the H content and H/C molar ratio in char_{x-y} obtained by elemental analysis are listed in Table 5. It can be seen from the table that as pressure increases from 0.1 MPa to 1.5 MPa, the H content in char gradually decreases and pressure promotes the release of H during the pyrolysis process. The CH₂/CH₃ in Naomaohu coal is high [20,43], indicating that there are more cyclic hydrocarbons or longer aliphatic chain hydrocarbons in the coal. These structures are prone to polycondensation during pyrolysis to generate aromatic hydrocarbons or break to form small molecular alkanes. It is more easily for unstable aliphatic chain hydrocarbons to decompose under pressurized conditions. Studies have shown that the difficulty of decomposition of O-containing functional groups is as follows: hydroxyl and non-reactive oxygen groups > carbonyl > phenolic hydroxyl > carboxyl [36]. It can be seen from Fig. 12(b) that the relative content of oxygen-containing functional groups has no obvious change rule with pressure, but the O-containing functional groups easily decomposed are converted into that not easily decomposed and stored in the char.

3.4.3. Release characteristics of gases and distribution characteristic of tar components

To demonstrate the two mechanisms of pressure, relevant experiments are conducted on the P-MFBRA and PPY-GC/MS, and the results



Fig. 12. (a) XPS original spectrum of $\mathsf{char}_{x\cdot y}$ and (b) C1s XPS peak area of $\mathsf{char}_{x\cdot y}.$

are shown in Figs. 13 and 14. The variation of total gas yield with pressure on the P-MFBRA is shown in Table A1. It can be observed that although the reactors are different, the influence of pressure on the pyrolysis process of Naomaohu coal is consistent, which is promoting effect first and then inhibiting effect. And the results of total gas yield on the P-MFBRA are consistent with that on the PPY-GC/MS, which can prove the assumption of Section 3.1. When the temperature is 600 °C,

 Table 4

 Surface functional group types and binding energy

Surface functional group types and Sinang chergy.					
Band Structure	Binding energy (eV)				
C=C and C-C	284.6 ± 0.3				
C-H	285.3 ± 0.3				
C-O	286.1 ± 0.3				
0-C-0/C==0	287.6 ± 0.3				
0-C==0	288.6 ± 0.3				

Table 5

Mass content of H in chars and H/C molar ratio.

T (°C)	P (MPa)	H/%	H/C mol
600	0.1	2.39	0.3751
	0.5	2.21	0.3456
	1.0	2.10	0.3268
	1.5	2.05	0.3189
700	0.1	1.80	0.2742
	0.5	1.72	0.2598
	1.0	1.45	0.2184
	1.5	1.39	0.2092
800	0.1	1.53	0.2292
	0.5	1.32	0.1949
	1.0	1.30	0.1917
	1.5	1.17	0.1714

the intensity of the secondary reaction is low, the reaction time of the gas is shortened, and the promoting effect of the pressure is greater than the inhibiting effect. The reaction is faster in the P-MFBRA than in the P- TGA, eliminating the influence of time. So as the temperature is 800 °C, the reaction time and the escape rate of the gas both increase first and then decrease, and it can be observed to a pronounced tailing due to the strengthening of the secondary reaction. As the pressure increases, the inhibitory effect is more pronounced at high temperature. In the P-TGA, the reaction time has a certain influence on the slow pyrolysis, So as the pressure increases, the pressure increases are pressure increases.

It can be seen from the above that the inhibiting effect of pressure at high temperature is more obvious, so in order to verify the promoting effect of pressure, the pyrolysis experiments under different pressures at 600 °C are carried out on PPY-GC/MS. The distribution of product yield and analysis of main components of tar are shown in Fig. 14. With the increase of pressure, the tar yield first increases and then decreases, gas yield increases and char yield first decreases and then increases. It is proved that the pressure increases from 0.1 to 2.0 MPa, the pressure first promotes the release of volatiles, and then inhibits the release of volatiles and enhances the secondary reaction of tar. Fig. 14(b) shows the variation of tar composition with pressure. With the increase of pressure, the content of aliphatic hydrocarbons (HCs) of C5-C9 and monocyclic aromatic hydrocarbons (MAHs) increase from 9.60% and 16.31% at 0.1 MPa to 18.80% and 27.87% at 2.0 MPa. The elevated contents of polycyclic aromatic hydrocarbons (PAHs) and C10-C22 at 1.0 MPa are attributed to the promoting effect of pressure. The escape rate of volatiles is accelerated under low pressure, so the tar content also increases briefly. When the pressure increases to 2.0 MPa, the PAHs undergo secondary cracking to generate more MAHs. Meantime, the cyclization of hydrocarbon groups increases the content of benzene and its homologues. The structure of non-hydrocarbon components is more unstable



Fig. 13. Release characteristics of gases under different temperature (a) 600 °C and (b) 800 °C.



Fig. 14. (a) The yield of pyrolysis products under different pressures at 600 °C and (b) Distribution of the main types of compounds in tar at 600 °C.

and prone to secondary reactions, so the content of oxygen-containing functional groups and phenolic substances tends to decrease with the increase of pressure, and the gas yield gradually increases. Experiments on P-MFBRA and PPY-GC/MS further confirmed the two action mechanisms of pressure.

3.5. The possible mechanisms of pressure on pyrolysis process

Combined with the network of volatiles secondary reactions proposed in the literature [44] and the above research results, the mechanism diagram of the pressure on the Naomaohu coal pyrolysis process is obtained (Fig. 15). Pressure mainly affects the pyrolysis process by affecting the secondary reaction of the primary volatiles in the particle. The pyrolysis process mainly includes primary and secondary pyrolysis, including (1)-(12), where (1)-(3) represent primary pyrolysis processes, and (4)-(12) represent secondary pyrolysis processes. In the process of leaving the semi-coke particles, the primary volatiles will undergo secondary pyrolysis, which can be summarized as the secondary pyrolysis inside the particles and the secondary pyrolysis outside the particles. The BET and SEM analysis showed that pressure increased the probability of secondary pyrolysis inside the particles. At atmosphere, the diffusion of gas is caused by the concentration gradient called the normal diffusion process. When (7) and (9) reach equilibrium, the tar vapor escapes from the interior of the coal particle. Whereas, at pressurized condition, the diffusion of gas is no longer the normal diffusion process. The increase of external pressure prolongs the residence time of volatile precursors inside the coal particles, intensifying the cracking reaction and producing more gas products, which increases the internal pressure. Once the internal pressure exceeds the external pressure, forced convection will be formed. Compared with normal diffusion, the mass transfer rate of forced convection is faster and more efficient, so that (4)-(9) are strengthened, especially the escape of (7) and (9). Ultimately, as the pressure increases, gas and tar yields increase, and char yield decreases.

However, as the external pressure continues to rise, it becomes more and more difficult for the internal volatiles to diffuse from the particles. and this inhibitory effect will increase the concentration of internal volatiles and enhances the secondary reaction of the primary volatiles in the particle. When the external pressure is higher than a certain critical value, and the internal pressure is insufficient to form forced convection, the inhibitory effect prevents the volatiles from escaping in the coal pores, and the secondary reaction of the primary volatiles in the particle is enhanced to generate carbon deposition. Process (10) is greatly intensified while (7) and (9) are suppressed, resulting in an increase in the yield of gases and char and a decrease in the yield of tar. The critical pressure value from promotion to inhibition is related to temperature, mainly because temperature is the main factor affecting the secondary reaction of coal pyrolysis.

4. Conclusions

In this paper, the effect of different pressures on coal pyrolysis characteristics during slow pyrolysis is studied on the P-TGA, and the mechanism of pressure is verified by combining P-MFBRA and PPY-GC/MS. The influence of pressure on char yield and physical properties is reflected in both promotion and inhibition, and the inhibition effect is more obvious with the increase of temperature. As the pressure increases, the char yield first decreases and then increases, and at 600 °C and 800 °C the minimum yields are in 1.0 MPa and 0.1 MPa, which are 57.48% and 54.04%, respectively. The S_{BET} of char increases first and then decreases. At 800 °C, the S_{BET} of char increases from 7.86 m²/g at 0.1 MPa to 19.81 m²/g at 0.5 MPa and then decreases. The effect of pressure on the chemical properties of char is relatively simple. As the pressure rises, the content of functional groups in char reduces and the degree of graphitization enhances.

Through the TG-DTG curve, XPS test, experiments on the P-MFBRA and PPY-GC/MS, it can be seen that the pressure mainly affects the pyrolysis process by affecting the secondary pyrolysis of the primary volatiles and is related to temperature. BET and SEM tests showed that the pressure increased the secondary pyrolysis of primary volatiles inside the particles. The main mechanisms are as follows. When the pyrolysis temperature is lower, the intensity of the secondary pyrolysis is weaker. As the external pressure is low, the forced flow of gas promotes the rapid escape of volatiles and accelerates the pyrolysis process. As the external pressure is high, the escape of volatiles is inhibited and the secondary pyrolysis process of primary volatiles inside the particles is strengthened. When the pyrolysis temperature is higher, the secondary pyrolysis is greatly enhanced, resulting in the inhibition effect of pressure is greater than the promotion effect under low pressure. The next experiment needs to explore the specific mechanism of pressure on the secondary reaction process.

CRediT authorship contribution statement

Zhu Yao: Experimental methods, Data processing, and Writing. Wang Qinhui: Experimental design, Communication. Yan Jiqing:



Fig. 15. Schematic diagram of the pressurized pyrolysis mechanism of Naomaohu coal.

Experiment. **Cen Jianmeng:** Communication. **Fang Mengxiang:** Data analysis, Language modification. **Ye Chao:** Language modification.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jaap.2022.105682.

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