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Research Article

The influence of pressure and temperature on coal pyrolysis/gasification[†]

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ABSTRACT: The aim of the study is mainly to understand the effect of pressure and temperature on the property of coal particles in pyrolysis/gasification. The pyrolysis of Shenfu (SF) coal sample and the gasification of resultant char were carried out in a thermogravimetric analyzer (TGA) under pressurized and ambient conditions. The gas released from coal pyrolysis was analyzed using a portable FTIR spectrometer connected to the TGA. Simultaneously, the surface structure and main chemical compounds of the pyrolyzed char particles were analyzed using gas sorption (ASAP2020), CNHS, etc. analysis instruments. First, the pyrolysis of SF coals was carried out in a pressurized TGA at various pressures (0.1, 0.8, 1.5, 3 and 5 Mpa) with a heating rate of 10 °C min^{-1} and a final temperature of 1000 °C. It was observed that higher pressures accelerated the devolatilization of coal samples at lower temperatures (<500 °C), while the maximum mass loss rate was reduced, and the solid char yield increased with increasing pressure. The specific surface area and chemical components changed with changing system pressure. The gasification reactivity of the solid char particles obtained was analyzed using ambient thermal balance at 1000 °C, using CO_2 as the gasifying agent. The gasification reactivity increased with increasing pyrolysis pressure. Then the pyrolysis of SF coal was carried out under different temperatures (500, 650, 800 and 1000 °C) at ambient and higher pressures (3 Mpa). With increasing temperature, the gas product from coal pyrolysis enhanced greatly at the expense of decreasing charcoal residue. The surface area of the char particles obtained were minimum at 800 °C (ambient pressure) and at 600 °C (3 Mpa). The gasification reactivity of solid charcoal residues decreased considerably with increasing pyrolysis temperature at ambient pressure, while at 3 Mpa a different result was obtained, with the highest gasification reactivity at 800 °C. © 2007 Curtin University of Technology and John Wiley & Sons, Ltd.

KEYWORDS: coal pyrolysis; char gasification; temperature; pressure

INTRODUCTION

Owing to the gradual decrease of fossil fuel reserves and the mounting concern over environmental pollution, advanced clean coal technologies have attracted increasing interest to attain high efficiency and low pollutant emissions. Coal gasification, as the most promising one, will play a vital role for energy utilization in the near future.

Coal gasification is a very complex process; it consists of coal pyrolysis and char gasification. Pyrolysis is the first step in the thermal-chemical conversion of coal; it involves a set of complex reactions. The gasification reactivity of coal greatly depends on the reactivity of coal char obtained from coal pyrolysis (Cloke *et al*., 1997). The gasification reactivity of the char is influenced by many factors, such as the coal type, pressure, final temperature, residence time, etc. Cloke *et al*. pointed out that the characteristics of the original coal have a significant influence on the property of coal pyrolysis and char gasification, but they also affect the influence of the operating condition on the behavior of coal utilization (Cloke *et al*., 1997; Alonso *et al*., 2001a). Many researchers have shown that char reactivity increases with increasing final temperature (Alonso *et al*., 2001b; Wall *et al*., 2002a; Harris *et al*., 2006), but some believe that an optimum temperature for each different coal sample exists (Ndaji *et al*., 1997; Cui *et al*., 1999). The char structure changes greatly with increasing pyrolysis pressure, thereby switching the gasification, so the gasification reactivity also shifts greatly (Sun *et al*., 1997).

In this study, the pyrolysis of a typical industrial bituminous coal sample – Shenfu (SF) coal – was carried out at different pressures and final temperatures using a pressurized thermogravimetric analyzer (TGA), and

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then the gasification property of the observed char was investigated using an ambient thermal analyzer (TA). At the same time, the surface structure and the chemical components of solid char were analyzed with gas sorption (ASAP2020) and CNHS elemental analyzers. The study is significant for the understanding of pressurized coal gasification, and it is essential for the development of coal gasification technology.

EXPERIMENTAL

Samples

In this study, a typical Chinese industrial coal – SF coal – was selected for analysis of the influence of pyrolysis pressure and final temperature on coal pyrolysis and char gasification. The original sample was ground and sieved with a 100-mesh screen, i.e. the samples analyzed were less than 100 mesh. The results of the proximate and ultimate analyses of the coal samples are listed in Table 1. SF coal appears to contain a high volatile content and a fixed carbon content, which are characteristics of bituminous coal.

Experimental apparatus and method

The pyrolysis of coal sample

Temperature-programmed pyrolysis experiments were performed in a pressurized TGA (TG Thermal Max 500, Thermal Cahn, USA). The schematic is shown in Fig. 1. Pure N_2 was used as the furnace gas and the purge gas to protect furnace parts and the balance. For coal pyrolysis, Ar was used as the reaction gas to keep the inert atmosphere. The flow rates of the three gases were kept similar. A back regulator was used to adjust the exhaust gas to maintain the system pressure. The apparatus has operating limits of 1100 °C and 10 Mpa. At 1000 °C, it can operate at 6.7 Mpa. To maintain safety, all tests were conducted at below 1000 °C and 5 MPa. The rate of mass loss was recorded as a function of temperature or time, and the different compounds evolved during pyrolysis were analyzed by means of a gas-phase Fourier transform infrared (FTIR) spectrometer.

To choose a reasonable sample mass and mitigate the effects of the cubicle under different pressures, two pre-experiments were conducted: (1) experiments by varying the sample mass (20–1000 mg) at ambient

Table 1. Proximate and ultimate analyses of coal sample.

	Proximate analysis (wt%)				Ultimate analysis (wt%, ad)				
	M_{ad}	V_d	A_d	FC_{daf}	C_{daf}	H_{daf}	N_{daf}	S_d	$O_{daf}{}^a$
SF	10.19	37.66	6.5	62.34	80.53	4.8	0.89	0.37	13.38

[a] O content was calculated by difference, ad: on air dried basis, d: on dried basis, daf: on dried and ash free basis.

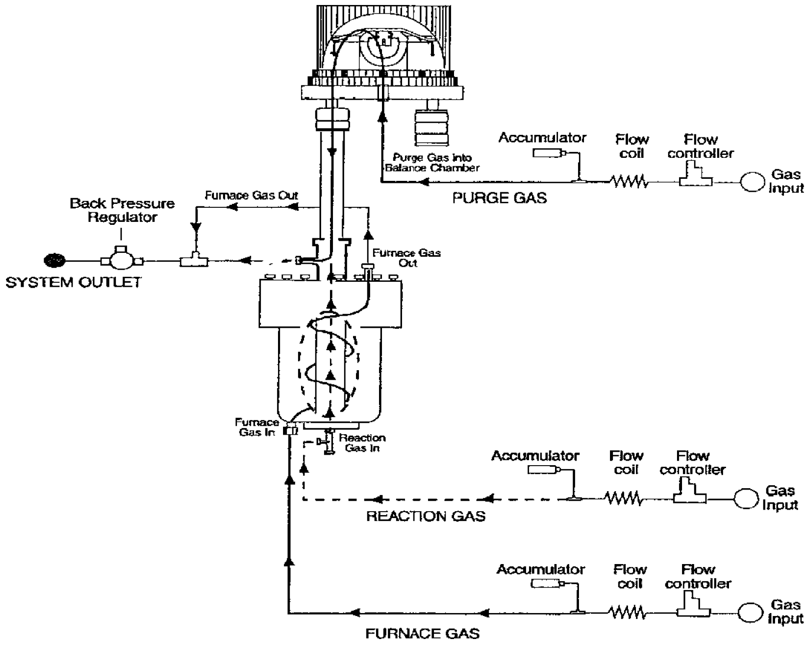

Figure 1. The flow scheme of the pressurized TGA.

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pressure with Ar (100 ml min^{-1}) as the protective gas; and (2) experiments by varying operating pressures (0.1–5 Mpa) without the sample. The detailed results are not presented owing to limitations of space. Here, only a brief description is given. Varying the initial sample mass in the range of 100–1000 mg has no significant influence on SF coal pyrolysis at 100 ml min^{-1} of flow rate, although, when the sample size was lower (20 mg), the pyrolysis of the shell moved largely to higher temperatures. It indicated that mass and heat transfer inside sample particles is negligible with the sample mass changing from 100 to 1000 mg. A mass of 1000 mg (a large size) was therefore chosen in this study in order to investigate the structure property of the resultant char in detail. As regards the system pressure, the weight of the empty cubicle increased from 20 to 100 mg as pressure increased from 0.1 to 5 Mpa, the weight increasing mainly at temperatures lower than 400 °C. In comparison with the sample size used in each trial, the side effect is great and cannot be neglected. To mitigate the influence caused by the sample cubicle at various operating pressures, the trial at selected pressures without sample was taken as the background, and subtracted during the following experiment.

The experimental procedure is briefly as follows. The sample (~1 g) was placed in the furnace hold in a quartz crucible. The flow rates of the three gases were set at 1 l min^{-1} separately to elevate the system pressure to the set value (0.1, 0.8, 1.5, 3, 5 Mpa). After that, the gas flow rate was adjusted to 100 ml min^{-1}, which was maintained during the whole experiment. Then the furnace was heated up to 1000 °C from ambient temperature at the rate of 10 °C min^{-1}, and kept there for 10 min to make sure that the pyrolysis was completed. The furnace was then cooled down quickly and the system pressure was slowly decreased to ambient. The solid charcoal residue was collected for further analysis. In each trial, the operating pressure was kept constant, and a back-pressure regulator was employed to control the system pressure. For pressurized trials, the gas product was exhausted out intermittently to keep the operating pressure constant.

With regard to the influence of the final temperature of pyrolysis, SF coal was pyrolyzed at four different temperatures (500, 650, 800 and 1000 °C) to check the interaction of pressure and temperature at the two different pressures involved (ambient pressure and 3 Mpa). Other operating conditions were kept the same as in the series of pressure trials.

With coal being heated up, the volatiles evolved, the evolving property varying with different pyrolysis pressures. To check the gas product evolution behavior online, the gas products released from the TGA were analyzed quantitatively using a portable FTIR spectrometer (pFTIR, Temet Gasmet DX-400, Finland) provided with a mercury cadmium telluride detector (MCTD) and a Calcmet workstation. The transfer line and the gas cell were heated to an initial temperature of 180 °C to avoid condensation or adsorption of semivolatile products. Each IR spectrum was obtained in 20 s and the IR scanning range was from 4000 to 500 cm^{-1}.

The analysis of solid char

With the volatiles evolving, a large number of pores were formed on the surface and inside the coal sample. To check the physical structure of the char sample, the surface area and pore structure of solid charcoal were examined quantitatively using a Micromeritics accelerated surface area porosimetry (ASAP 2020, USA) auto-adsorption analyzer to obtain N_2 adsorption isotherms at 77 K. The specific surface area and average pore size of the resulting char from coal pyrolysis were explored in detail. Simultaneously, the ultimate analysis of the char samples was carried out using an elemental analyzer, Vario EL II CNHS/O (Germany), to obtain the difference in the main organic components (C, H, O, N, S) of the solid charcoal observed under different pyrolysis pressures.

The gasification of solid char

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

Isothermal char gasification experiments were performed with a thermobalance (STA 409C, Netsch Germany) in a carbon dioxide atmosphere at 1000 °C. About 20 mg of charcoal obtained after the pyrolysis was charged into an alumina container, which was then placed on the thermal balance. As soon as the sample was heated to 1000 °C at 50 °C/min in a flow of high-purity Ar (100 ml min^{-1}), Ar was switched to pure carbon dioxide (100 ml min^{-1}) to start char gasification, and this was maintained for 60 min to make sure the gasification of chars was completed.

With the gasification proceeding, the char mass lost quickly. Takarada pointed out that the reactivity exponent (R) can be used to analyze the gasification reactivity, and it was successfully used to investigate the gasification reactivity of 34 different coal samples quantitatively (Takarada *et al*., 1985).

$$R = \frac{2}{\tau_{0.5}}, (\text{h}^{-1}) \tag{1}$$

where $\tau_{0.5}$ is the time (h) for the carbon conversion ratio reaching 50%. A larger R means higher gasification reactivity of the charcoal. Here, it was used to display the gasification reactivity of solid charcoal observed from coal pyrolysis under different conditions.

RESULTS AND DISCUSSION

The influence of pyrolysis pressure

The influence of pyrolysis pressure on coal pyrolysis

The TG and DTG curves of SF coal pyrolysis at different pressures are plotted in Figs 2 and 3. From the two figures, it can be observed that the pyrolysis of coal can be divided into four ranges. When temperature is lower than 200 °C, it is mainly moisture removal; in the evolved gas, some H_2O was found using FTIR. With the temperature increasing further (300–400 °C), no obvious weight loss was found from the TG curve; just trace CO_2 was detected in the gas product, with no obvious decomposition prior to primary pyrolysis. With further increase in temperature (>400 °C), the primary pyrolysis took place. The DTG curve shows the mass loss rate peak (400–700 °C). The weakest bonds may break to form molecular fragments. Functional groups also are decomposed and released out in the gas species, and they are mainly CO_2, CO, light aliphatics, CH_4 and H_2O, etc. (refer to Fig. 4 for the typical IR spectra of gas product from coal pyrolysis). At temperatures higher than 700 °C, another peak was displayed (~800 °C). The reactions that took place were mainly from condensation of the carbon matrix, with the evolution of CO and H_2.

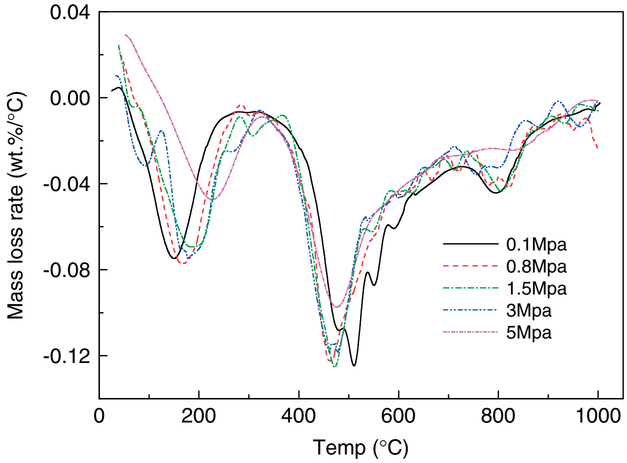

Figure 3. The DTG curves of SF coal pyrolysis under different pressures. This figure is available in colour online at www.apjChemEng.com.

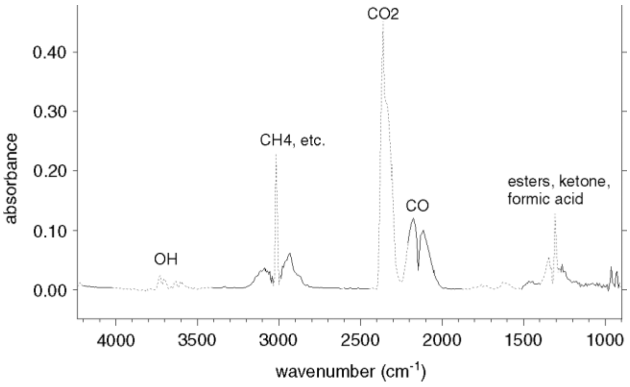

Figure 4. The typical IR spectra of the gas product from coal pyrolysis.

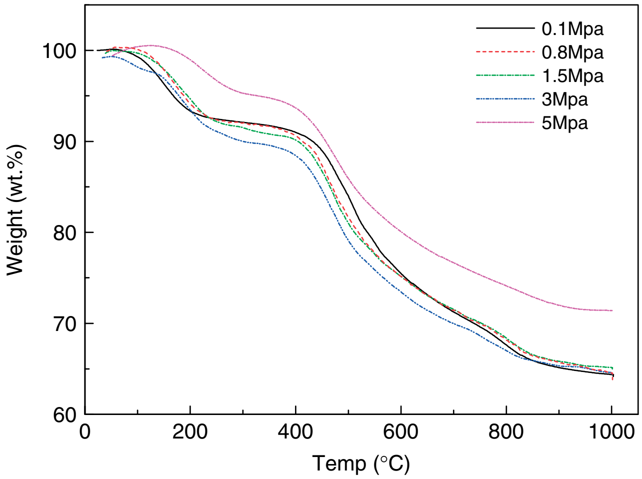

Figure 2. The TG curves of SF coal pyrolysis under different pressures. This figure is available in colour online at www.apjChemEng.com.

From the pyrolysis curves (TG and DTG), the influence caused by the sample cubicle under different pressures was subtracted. From the two curves, it can be observed that moisture removal was inhibited and moved to a higher temperature with the pressure increasing from ambient to 5 Mpa. The higher external pressure might impede the release of water. With respect to the volatiles removal, a different trend was displayed from the drying stage. The devolatilization process shifted to lower temperatures with pressure increasing from ambient to 3 Mpa, and following that, the pyrolysis curves moved to higher temperatures with pressure increasing further to 5 Mpa. The solid residue after coal pyrolysis increased, especially for 5 Mpa, and the yield increased greatly (~6 wt%). There are two peaks displayed in the DTG curves of the coal pyrolysis. The first peak of SF coal pyrolysis is located at ~500 °C and is caused by the primary pyrolysis of the SF coal. When the temperature is lower than 500 °C, the mass loss rate increases; the higher fluidity of coal at the higher pressure might be the main reason. However, the temperature and the peak value decreased slightly with increase in pressure. The second peak located at

~800 °C might be attributed to the secondary pyrolysis (the cracking of the interior tar). The peak value decreased greatly with increase in pressure, and it might be attributed to the higher pressure that suppressed the evaporation and cracking of liquid tar; however, higher pressures extend the residence time of the gas product, enhancing the cracking of hydrocarbon, and hence more light gas products are formed as confirmed by the FTIR results (result not shown).

From the TG curves, it can be seen that the total volatile yield decreased with increasing pressure, whereas the solid charcoal yield increased. From the point of view of the constant system mass, it can be deduced that the tar yield would decrease greatly with increasing pressure. The mechanism of the effect of pressure on coal pyrolysis is the enhanced secondary reactions and mass transportation at high pressures. It is consistent with previous research, which show that the total volatile and tar yields decrease with increasing pyrolysis pressure, whereas the gas yield increases with pressure (Cloke *et al*., 1999; Wall *et al*., 2002b).

As mentioned above, higher pressures extended the residence time of the volatiles, and are favorable for the thermal cracking of tar; thus the compounds of the char vary with pyrolysis pressure. The ultimate analysis of the solid charcoal residue is listed in Table 2. It showed that the C content increased while the H content decreased slightly with increasing pressure, and hence the molar ratio of C/H increased significantly with increasing pyrolysis pressure, i.e. more H compound evolved. It confirmed the result that a higher pressure is favorable for the secondary pyrolysis of the volatiles, and more H-containing gas products are formed.

The BET surface area and the average pore diameter are listed in Table 3. It can be seen that the specific surface area increased with pressure and reached the maximum value when the pyrolysis pressure was at 0.8 Mpa. After that, the specific surface area decreased with further increase in pressure. The mean pore size showed the reverse tendency to the BET surface area. It indicated that the pressure increased the fluidity of the coal particle and favored the formation of porous char, which increased the surface area. When the pressure is higher than 0.8 Mpa, the swelling of the solid sample becomes strong, and more tar residue is left on its surface, so that the pore opening in the char particle was blocked and the BET surface area is reduced.

Table 2. The ultimate analysis of solid charcoal at different pressures (daf).

Char sample	C (wt%)	H (wt%)	N (wt%)	S (wt%)	C/H (mol)
0.1 MPa	87.76	0.53	0.78	0.58	13.75
0.8 MPa	88.69	0.42	0.80	0.65	17.63
1.5 MPa	88.61	0.40	0.80	0.65	18.30
3 MPa	89.63	0.40	0.83	0.62	18.80
5 MPa	89.43	0.37	0.80	0.64	20.29

The influence of pyrolysis pressure on char gasification reactivity

The pressure at which the parent coal is devolatilized also plays an important role in the gasification reactivity of the resulting char. The gasification profiles of solid char obtained from SF pyrolysis at different pressures is plotted in Figs 5 and 6 in TG (wt%) as well as DTG (wt%/min). When temperature is lower than 1000 °C, which is the post-pyrolysis stage, there is just some external moisture removal and tar residue release; however, since the heating rate is very fast and the post-pyrolysis period very short, it is not enough for tar residue removal, and no obvious weigh loss is observed. As temperature is increased to 1000 °C, the carrier gas was switched to CO_2 and the gasification of solid char started. With extended reaction time, solid charcoal reacted with CO_2 quickly. From the

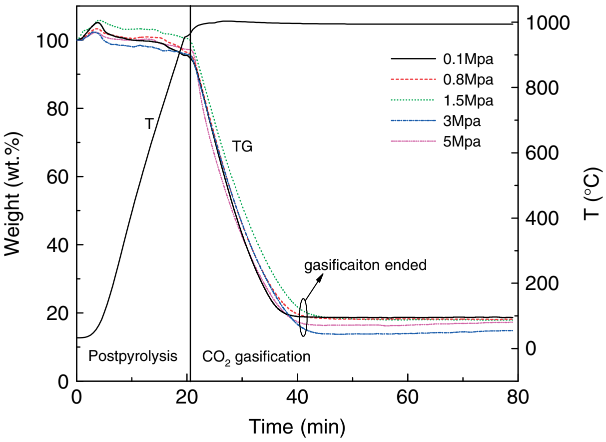

Figure 5. The TG curves of the gasification of char observed under different pressures. This figure is available in colour online at www.apjChemEng.com.

Table 3. The specific surface area of char from coal pyrolysis under different pressures.

Pressure (MPa)	0.1	0.8	1.5	3	5
S_{BET} ($m^2\ g^{-1}$)	0.7366	3.9841	2.0058	1.8731	1.5046
Diameter (Å)	250.551	155.4419	179.2621	149.7015	194.1895

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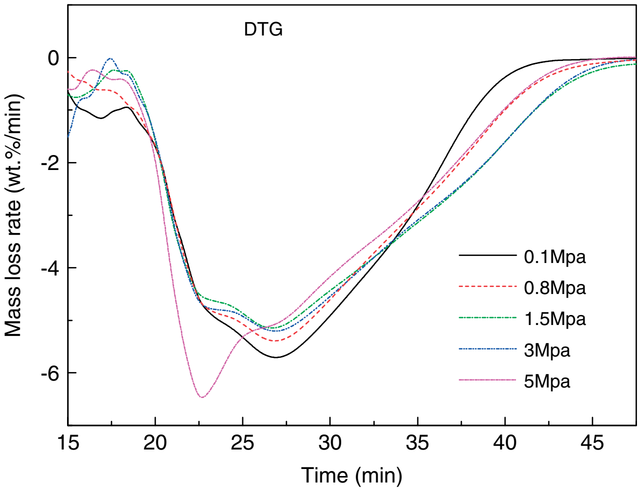

Figure 6. The DTG curves of the gasification of char observed under different pressures. This figure is available in colour online at www.apjChemEng.com.

Table 4. The reactivity exponent of charcoal gasification.

Pressure (Mpa)	0.1	0.8	1.5	3	5
R (h^{-1})	1.74	4.08	3.60	3.90	4.68

gasification curves, it can be seen that the gasification reaction was completed in 25 min (from 20th min to 45th min, refer to Fig. 5) with some ash residue. No obvious weight loss was detected with further extension of time. In the initial stage (from 20th to 22.5th min in Fig. 5), the gasification was accelerated with increasing pyrolysis pressure, especially for 5 Mpa. It might be attributed to more hydrocarbon residue on the solid char surface at higher pressures. It might act as the active point to encourage the gasification of solid carbon. After that, the gasification rate is hindered by the pyrolysis pressure (from 23rd to 35th min, refer to Fig. 5), except at the pressure of 5 Mpa. With the retention time going to the final stage (from 35th to 45th min), the higher pressure increased the gasification rate of solid charcoal. It might be caused by the reaction of char and CO_2, shift in the tar residue and more open pores, thereby enhancing the gasification rate of the char residue. The gasification activity of solid char is calculated using Eqn (1), and the reactivity exponent was calculated on the basis of the carbon conversion in the range of 20–80% (Zhou *et al*., 2002). The results are listed in Table 4. It can be seen that the value of R increases greatly with the pressure increasing from ambient to 0.8 Mpa, and it might have been caused by the larger surface area of the solid char and the favorable diffusion of the gasifying agent CO_2 and the liberation of the gas product. With pressure increasing further to 1.5 Mpa, R decreased to 3.60 h^{-1}, and it might be attributed to the decrease in surface area, lowering of the diffusing and evolving velocity and, consequently, slow gasification (refer to Fig. 5). However, the value of the exponent is increased, i.e. the gasification process is accelerated, with pressure increasing from 1.5 to 5 Mpa, and the higher tar residue covering the surface of the char might be the main reason for this. The CO_2 shifting of the volatile residue might activate the reaction between carbon and CO_2. However, the diffusion of CO_2 and the evolution of the gas product (CO) were impeded by the decrease in the surface area of the solid char particles. The variation of the reactivity of char gasification is the combined result of the influence of surface structure and the chemical component. The mechanism in detail will be studied in the near future.

The influence of pyrolysis temperature

The pyrolysis of SF coal at the selected temperatures finished promptly, even at a lower temperature of 500 °C. The pyrolysis curves of the coal sample at different temperatures are not shown. From the pyrolysis curves, it can be seen that the influence of temperature on coal pyrolysis at 3 Mpa is much stronger than at ambient pressure, as no obvious weight loss was observed in isothermal period with coal pyrolysis at 3 Mpa, while about 2–3 wt% more weight loss for SF coal was shown in isothermal period at ambient pressure. It might be because the higher pressure suppressed the evolution and re-forming of the volatiles. The solid char yield is listed in Table 5. It can be seen that the solid char yield decreases greatly with the final temperature increasing, and that the solid char yield increases with the pressure increasing from ambient to 3 Mpa at different temperatures, which is consistent with the previous result (refer to Fig. 2). The ultimate analysis result (Table 5) showed that the C content increased with increasing final temperature, while the H content decreased greatly; hence the molar ratio of C/H increased greatly with increasing temperature. It is indicated that more H compounds in the original coal evolved out with increasing pyrolysis temperature. N also decreased with increasing temperature, which might be attributed to the decomposition of the N compound at higher temperatures. With respect to the two pressure series (3 Mpa and ambient), it can be seen that the H contents of the former case all are lower than those of the latter case, and it confirmed the previous experimental result (refer to Table 3) that a higher pressure is favorable for hydrocarbon cracking and lighter H-containing compounds evolving. The molar ratio of C/H also increased greatly as the pressure increased from ambient to 3 Mpa, i.e. less H was left in the solid charcoal.

Table 5. The ultimate analysis of solid charcoal under different temperatures.

Char sample (°C)		Char yield (%)	C_{daf} (%)	H_{daf} (%)	N_{daf} (%)	S_{daf} (%)	C/H (mol)
Ambient pressure	500	78.78	81.04	3.42	1.12	0.68	1.97
	650	70.58	86.70	1.98	1.09	0.67	3.65
	800	64.56	89.07	0.99	0.90	0.41	7.51
	1000	63.23	87.91	0.53	0.78	0.58	13.75
3 Mpa	500	79.58	80.82	3.07	1.11	0.63	2.20
	650	71.87	87.71	1.99	1.07	0.52	3.67
	800	68.44	87.45	0.65	0.89	0.58	11.25
	1000	65.43	89.53	0.40	0.83	0.62	18.80

Table 6. The structure parameters of solid charcoal under different temperatures.

Temperature (°C)		500	650	800	1000
Ambient pressure	S_{BET} ($m^2\ g^{-1}$)	1.2599	0.4077	0.0555	0.7366
	Diameter (Å)	147.95	298.09	1464.35	250.55
3 Mpa	S_{BET} ($m^2\ g^{-1}$)	0.9982	0.057	0.14	1.87
	Diameter (Å)	145.78	1340.53	939.84	194.19

The parameters of the physical structure of the char particles are shown in Table 6. It can be derived that S_{BET} decreased greatly as temperature increased and attained the minimum value at 800 °C at ambient pressure and 650 °C at 3 Mpa. The evolution of internal organic compounds might be the major reason. With the sample heated up (>400 °C), a large amount of tar evolved; however, the temperature is not high enough for the thermal cracking of tar and some was left on the char surface and blocked some fine pores, thereby decreasing the pore area. A higher pressure (3 Mpa) accelerated the decrease rate, which attained the minimum value at a lower temperature (650 °C). After that, with increasing temperature, the tar started to crack, more light gas formed and evolved, fine pores opened and the surface area of char particles increased slightly.

The gasification curves of char at different temperatures are plotted in Figs 7–10. It can be observed that there is some weight loss for charcoal (500 and 650 °C) when the charcoal sample was heated up to 1000 °C quickly in the inert gas Ar, which is the post-pyrolysis period, due to the devolatilization of the volatile residue on the solid charcoal observed at lower temperature during the pyrolysis process. From Figs 7 and 8, it can be observed that the gasification of the resulting char was accelerated with decreasing pyrolysis temperature. The maximum mass loss rate was 5.7, 7.2, 8.9 and 11.9% $\min^{-1}$ for the four cases, respectively; the gasification time was shortened greatly. The fast gasification of the lower temperature char might be attributed to hydrocarbon residue on char particle surface. Different from the char observed at 1000 and 500 °C, the DTG curve of the char particles at 650 and 800 °C showed two obvious peaks in gasification period, and the value of the first peak increased with increasing pyrolysis temperature. The shifting of the tar residue covered on char surface by CO_2 during coal pyrolysis might give rise to fast gasification. After that, the pores open, CO_2 diffuses into the pores and the reaction between carbon and gasifying agent CO_2 starts; hence CO_2 is converted to CO and released. The gasification of char consists of CO_2 shifting of the tar residue and the gasification of solid char particles. From the two figures (Figs 6 and 7), it can be seen that 800 °C is optimum for the initial stage of char gasification, and a lower temperature (500 °C) is better for the whole gasification process.

Regarding the char observed at 3 Mpa, the gasification increased with temperature increasing from

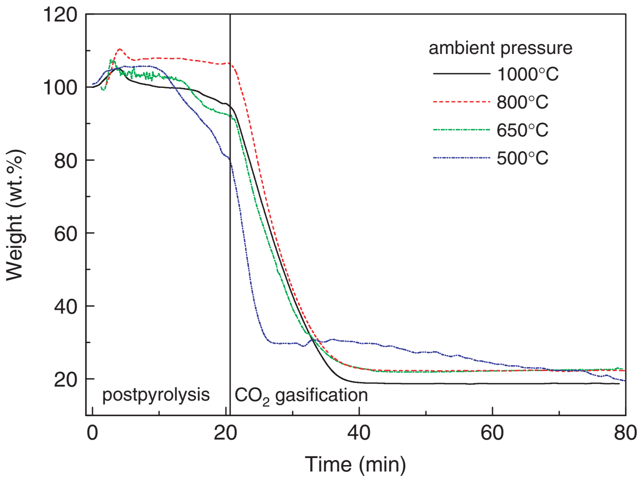

Figure 7. Gasification curves (TG) of charcoal observed under different temperatures (0 Mpa). This figure is available in colour online at www.apjChemEng.com.

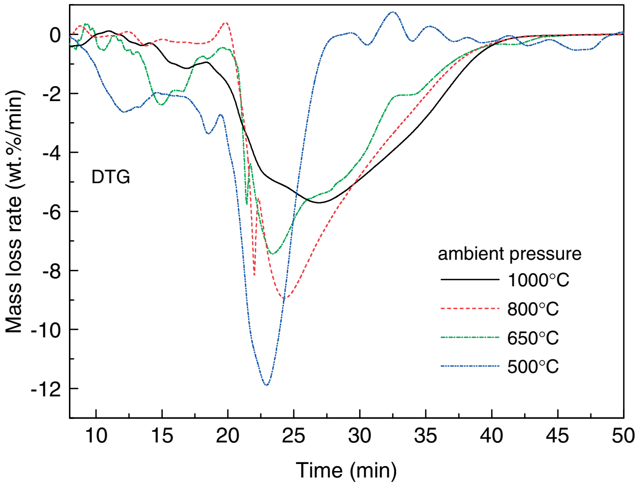

Figure 8. Gasification curves (DTG) of charcoal observed under different temperatures (0 Mpa). This figure is available in colour online at www.apjChemEng.com.

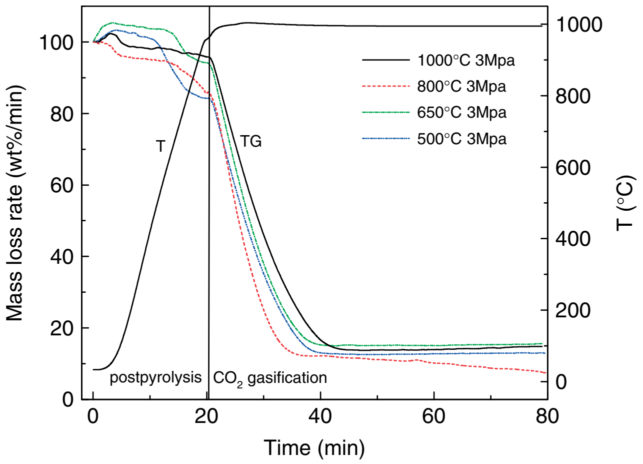

Figure 9. Gasification curves (TG) of charcoal observed under different temperatures (3 Mpa). This figure is available in colour online at www.apjChemEng.com.

500–800 °C, and then it decreased with the temperature increasing further to 1000 °C. There are two overlapping gasification peaks of the char (500, 650 and 1000 °C). The former might be the result of the thermal cracking of the tar residue; the latter belongs to the CO_2 gasification of carbon in solid char. For the char made and observed at 800 °C, only one sharp peak was displayed in the gasification curves. The gasification is fastest among the 3 Mpa batch. It is similar to that of 500 °C at ambient pressure. It might be the result of the higher gasification reactivity of the tar compounds covered on char surface; it showed great relation with char gasification reactivity.

The gasification exponent (R) of char from coal pyrolysis under different temperatures is listed in Table 7. It can be observed that R decreased with increasing temperature for char observed at ambient pressure, i.e. char observed at 500 °C with the highest reactivity. However, for the char at 3 Mpa, R decreased with the temperature increasing from 500 to 650 °C, and it might be attributed to the large shrinkage of the surface area and the decrease in the volatile residue of solid char particles. Thereafter, it increased to 5.75 h^{-1} with the temperature increasing to 800 °C, and it might be due to the formation of porous char with a higher specific surface area of the char particles, even volatile residue in solid char decreasing greatly. However, as temperature is increased further to 1000 °C, the value of gasification exponent decreased as the volatile release enhanced greatly. The surface area plays a vital role in char gasification as well production of the volatile residue. From Table 7, it can be seen that the char gasification showed the highest reactivity in the 3 Mpa batch when the final temperature of the coal pyrolysis was at 800 °C. When the two batches at ambient and 3 Mpa are compared, R decreased greatly at 500 and 650 °C with pyrolysis pressure increasing from ambient to 3 Mpa, which is similar to results of previous research (Sha *et al*., 1990; Wall *et al*., 2002a). At lower temperatures (>650 °C), the tar residue on char particles is very high, while the surface area is very low, and the influence of specific surface area plays the main role in char gasification; however, with temperature increasing further to 800 and 1000 °C, the gasification reactivity increased

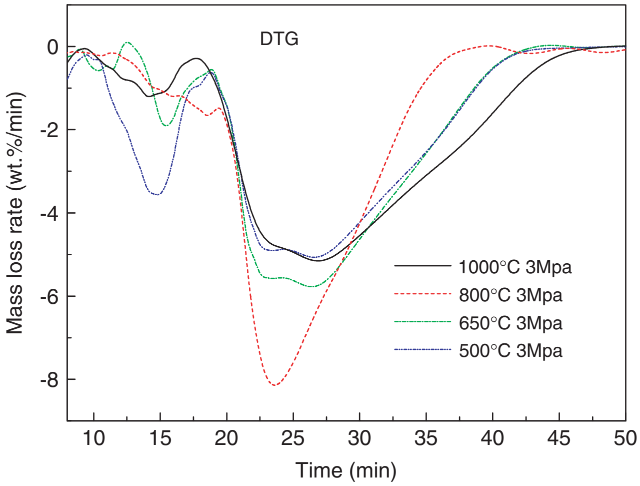

Figure 10. Gasification curves (DTG) of charcoal observed at different temperatures (3 Mpa). This figure is available in colour online at www.apjChemEng.com.

Table 7. Gasification exponent of char from coal pyrolysis at different temperatures.

	Temperature (°C)	500	650	800	1000
R (h^{-1})	Ambient pressure	11.1	4.86	5.15	1.74
	3 Mpa	5.34	4.74	5.75	3.90

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with increasing pressure, which might be attributed to the tar residue caused by the higher pyrolysis pressure. The influence of the pyrolysis temperature on char structure and gasification reactivity varied with pressure, which indicated that there is strong interaction between temperature and pressure (Cai *et al*., 1996). The variation of the behavior of char gasification is the result of the chemical structure (tar residue) and physical structure (pore structure) together; however, the physico-chemical property of char changed with the pyrolysis condition, such as pressure, temperature, etc. The mechanism will be investigated in depth in the near future.

CONCLUSIONS

The influence of operating pressure and final temperature on the property of coal pyrolysis, and the gasification behavior of resultant char were investigated using pressurized and ambient TGA with FTIR, ASAP2020, CNHS, etc. instruments. The following conclusions can be drawn:

1. The pyrolysis of coal mainly happened in two temperature ranges: 400–700 °C, the primary pyrolysis region with the evolution of CO_2, CO, light aliphatics, CH_4 and H_2O, etc; and 700–900 °C, the secondary pyrolysis region with CO and H_2 as the main gas products.
2. Pressure had a greatly influence on coal pyrolysis. The devolatilization rate was accelerated with increasing pressure when temperature was lower than 500 °C, whereas the maximum value of the weight loss decreased. The yield of solid charcoal increased with increasing pressure, especially at 5 Mpa. It might be attributed to the higher pyrolysis pressure that suppressed the release of volatiles; hence the carbon content increased while H content decreased straightly. The specific surface area increased greatly with the pressure increasing from ambient to 0.8 Mpa; after that it decreased greatly with the pressure increasing further. The gasification of the char is the combined result of the surface structure and chemical compounds of the char particles. Higher specific surface area and more tar residue on char particles are favorable for char gasification. The gasification of char particles enhanced with increased pressure.
3. The final temperature plays a vital role in coal pyrolysis, the solid char yield decreasing greatly with increasing temperature, while the C content increasing greatly and H content decreasing. The specific area decreased greatly as the temperature increased from 500 to 800 °C at ambient pressure and attained the minimum value, after which it increased greatly with the temperature increasing further. Higher pressure accelerated the decrease; with the pyrolysis pressure increasing from ambient to 3 Mpa, the minimum surface area was achieved at 650 °C. The gasification of char the particles consisted in the shifting of the tar residue and the C–CO_2 reaction. When the char particles were observed at ambient pressure, the gasification reactivity decreased with increasing pyrolysis temperature. When the pyrolysis pressure is 3 Mpa, the gasification of char showed the highest reactivity at a pyrolysis temperature of 800 °C. There exists a strong interaction between the pyrolysis pressure and the final temperature.

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