

Synthesis gas and char production from Mongolian coals in the continuous devolatilization process

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Abstract—Devolatilization of Mongolian coal (Baganuur coal (BC), Shievee Ovoo coal (SOC), and Shievee Ovoo dried coal (SOC-D)) was investigated by using bench-sized fixed-bed and rotary kiln-type reactors. Devolatilization was assessed by comparing the coal's type and dry basis, temperature, gaseous flux, tar formation/generation, devolatilization rate, char yield, heating value, and the components of the raw coal and char. In the fixed bed reactor, higher temperatures increased the rate of devolatilization but decreased char production. BC showed higher rates of devolatilization and char yields than SOC or SOC-D. Each coal showed inversely proportional devolatilization and char yields, though the relation was not maintained between the different coal samples because of their different contents of inherent moisture, ash, fixed carbon, and volatile matter. Higher temperatures led to the formation of less tar, though with more diverse components that had higher boiling points. The coal gas produced from all three samples contained more hydrogen and less carbon dioxide at higher temperatures. Cracking by multiple functional groups, steam gasification of char or volatiles, and reforming of light hydrocarbon gas increased with increasing temperature, resulting in more hydrogen. The water gas shift (WGS) reaction decreased with increasing temperature, reducing the concentration of carbon dioxide. BC and SOC, with retained inherent moisture, produced substantially higher amounts of hydrogen at high temperature, indicating that hydrogen production occurred under high-temperature steam. The continuous supply of steam from coal in the rotary kiln reactor allowed further exploration of coal gas production. Coal gas mainly comprising syngas was generated at 700-800 °C under a steam atmosphere, with production greatest at 800 °C. These results suggest that clean char and high value-added syngas can be produced simultaneously through the devolatilization of coal at lower temperature at atmospheric pressure than the entrained-bed type gasification temperature of 1,300-1,600 °C.

Key words: Mongolia Coal, Devolatilization, Syngas, Char, Rotary Kiln

INTRODUCTION

As alternative energy sources to oil are sought, widely available coal is receiving renewed attention. Low-rank coal has more stable prices, making it attractive to countries without petroleum reserves [1-3]. Recoverable reserves of brown coal are about 20%, and its recoverable life index is higher than that of soft coal [4]. Low-rank coals such as brown coal show low heating values and improvement of their quality is required for their more efficient use, since they are high in inherent moisture and ash and contain *ca.* 70% less carbon than high-rank coal. Drying and pyrolyzing low-rank coals can effectively increase their heating values by removing inherent moisture and increasing their carbon content. If the components and formation of the resulting coal gas can be appropriately controlled, then efficiency can be further enhanced and the products can be combined with processes such as liquefaction, DME combination, or fuel cells.

The pyrolysis of coal is an important part of combustion, gasification and liquefaction, and its reactions and kinetics have been studied [5]. Pyrolysis generally occurs at over 400 °C under anaerobic condi-

tions [6]. When coal is heated, its inherent moisture evaporates, and then coal gas comprising hydrogen, carbon monoxide, methane, carbon dioxide, and acetylene is generated by the pyrolysis of its volatile matter, tar is also generated. The char, with increased carbon content, created during pyrolysis can constitute a high-quality solid fuel depending on the remainder of volatile matter [7]. Devolatilization is affected by temperature [8], pressure [9], residence time [10], and the coal's composition [11]. When coals devolatilize at over 600 °C, syngas comprising H₂ and CO is produced alongside the coal gas. Liquid byproduct is generally produced below 600 °C, when devolatilization begins. As the reaction temperature increases, char and tar yields tend to drop [12,13].

Yurt dwellers near Ulan Bator, Mongolia use untreated low-rank coals as heating fuels, causing severe air pollution in the area. Therefore, interest in use of clean coal, which can improve air quality, is increasing. This study evaluates the devolatilization of coals from the Baganuur and Shievee Ovoo mines near the Mongol capital. To assess the effects of the coals' inherent moisture content on the devolatilization reaction, coal from the Shievee ovoo mine was dried (SOC-D) and devolatilized in the fixed bed reactor. Also, devolatilization in a rotary kiln reactor was conducted at higher temperature using BC containing inherent moisture, which was an optimized condition. Therefore, these results are suggesting that the produc-

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tion of coal gas comprising mainly hydrogen and carbon monoxide by devolatilization represents a more convenient method than gasification that requires high temperature and pressure. An inexpensive devolatilization device can also be used to liquefy coal, combine DME, or convert coal gas into fuel for fuel cells. Overall, the development of an efficient devolatilization process stands to add significant value to otherwise low-rank coal.

EXPERIMENTAL

1. Materials

BC, SOC, and SOC-D were crushed to *ca.* 3 mm and stored sealed from atmospheric moisture. SOC-D was dried for 24 hours at 105 °C before use. A TGA-701 (LECO) and a Parr 6320EF calorimeter (PARR) were used for the proximate analysis of the coals and their higher heating values, respectively. A TruSpec Elemental Analyzer (LECO) and an SC-432DR Sulfur Analyzer (LECO) were used for elemental analysis. Characteristics of the coals are listed in Table 1.

2. Devolatilization in a Fixed Bed Reactor

A lab-scale fixed bed reactor was used to evaluate characteristics of char, syngas and tar by changing the coal type and temperature parameters. Devolatilization in a fixed bed device (Fig. 1) was tested at temperatures up to 800 °C. The maximum capacity of the SUS reactor (170 mm high, 120 mm internal diameter) was 2 kg. A butterfly valve allowed coal to freefall into the reactor when its temperature reached a certain level. The devolatilization of 400 g crushed coal was tested at 600, 700, and 800 °C, adjusted by K-type thermocouples installed in the exterior and the interior of the reactor. N₂ carrier gas was constantly fed at 100 mL/min. A capturing device filled with four isopropanols connected in series in the latter part of the reactor was installed to capture the generated coal gas's tar and moisture. An ice bath maintained the capturing device at ≤4 °C [14]. The flux of the gas discharged after tar and moisture capture was measured with a wet flowmeter. The dry coal gas was then collected from the sampling port to assess its composition using a gas analyzer. When the reactor reached the desired temperature, the coal was allowed to fall into the reactor, where it was devolatilized for three hours. The devolatilization rate was calculated from the fol-

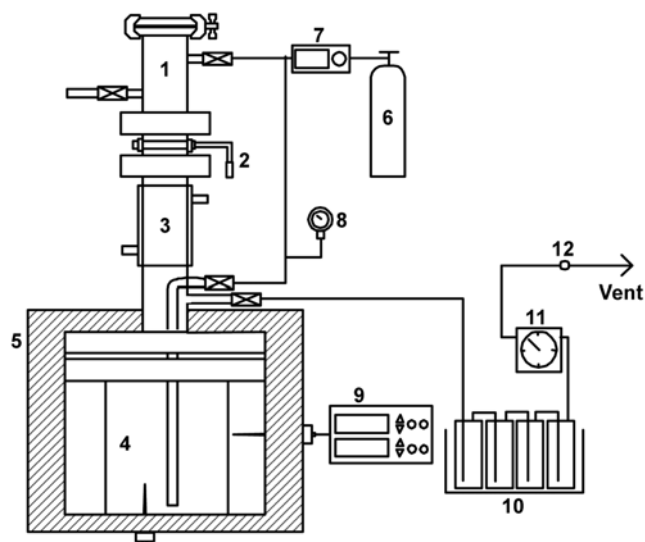


Fig. 1. Schematic diagram of the fixed bed reactor.

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|-----------------------|--------------------------------|-----------------------|
| 1. Coal storage place | 5. Furnace | 10. Tar trap |
| 2. Butterfly valve | 6. Purge gas (N ₂) | 11. Wet flowmeter |
| 3. Air cooling system | 7. Mass flow controller | 12. Gas sampling port |
| 4. Reactor | 8. Pressure gauge | |
| | 9. Thermo controller | |

lowing formula based on the results of the proximate analysis:

$$\text{Devolatilization rate} = \frac{W_{rc} \times F_{rc} - W_c \times F_c}{W_{rc} \times F_{rc}} \times 100 \quad (1)$$

Where, W_{rc} : Mass of raw coal

F_{rc} : Ratio of volatile matter in the raw coal

W_c : Mass of char generated after devolatilization

F_c : Ratio of the volatile matter in the char generated after devolatilization

The discharged coal gas was analyzed with an HP5890 gas chromatograph (GC) equipped with a Carbosphere column and TCD detector. The components of the tar captured in the tar trap were

Table 1. Proximate and ultimate analyses of raw coal and char samples

Samples	Proximate analysis (wt%, ARB)				Ultimate analysis (wt%, DB)				HHV (kcal/kg)
	M	VM	FC	Ash	C	H	N	S	
BC	29.29	28.93	35.86	5.92	65.23	5.38	0.35	0.28	5,202
BC600	0.56	23.09	65.37	10.98					
BC700	0.62	13.77	73.20	12.41					
BC800	0.54	7.84	77.99	13.63	79.90	1.02	0.92	0.31	6,662
SOC	37.11	23.98	25.13	13.78	54.33	3.93	0.39	0.44	5,030
SOC600	0.59	24.05	53.89	21.47					
SOC700	0.79	15.61	58.30	25.30					
SOC800	1.06	16.20	57.70	25.04	64.33	1.50	0.68	1.11	5,670
SOC-D	1.07	37.19	42.58	19.16	54.33	3.93	0.39	0.44	4,860
SOC-D600	0.45	17.34	57.68	24.53					
SOC-D700	0.55	13.64	59.40	26.41					
SOC-D800	0.73	7.65	64.59	27.03	72.10	0.71	0.75	1.13	6,010

*ARB: as received basis, DB: dry basis

analyzed by an HP5973 mass spectroscope (GC-MS) with a DB-5MS column (30 m×0.25 mm i.d.×0.5 µm film thickness). The injector and oven were set at 270 and 320 °C, respectively. The isopropanol and water solvents used for capturing tar were analyzed by using an Innowax column (30 m×0.32 mm i.d.×0.15 µm film thickness), which can detect isopropanol, water, light tar, and so on, with injector and oven both set at 230 °C.

3. Devolatilization in a Rotary Kiln Reactor

A rotary kiln reactor was used to scale-up and evaluate continual devolatilization characteristics at optimum conditions of a fixed bed reactor; the operating conditions of fixed bed and rotary kiln reactor are shown in Table 2. The rotary kiln supplied coal continuously with a maximum capacity of 30 kg/h. It consisted of a coal hopper, rotary kiln, kerosene burner, refractory material, char recovery system, and a motor for rotating the kiln (Fig. 2). The rotary kiln reactor was preheated to approximately 700 and 800 °C by two kerosene burners before coal was put into the reactor. Coal with continuous supply was devolatilized to char and then collected in the char receiver. At this time, reactor temperature was controlled by K-type thermocouples installed in the interior of the kiln. The

Table 2. Experimental conditions of fixed bed and rotary kiln reactor

1. Reactor	Fixed bed	Rotary kiln
2. Coal	BC	BC
	SOC	-
	SOC-D	-
3. Coal feeding rate (kg/h)	- ^a	15
4. Residence time (min)	180	30
5. Temperature (°C)	600, 700, 800	700, 800

^a0.4 kg of coal fall into the reactor at a time

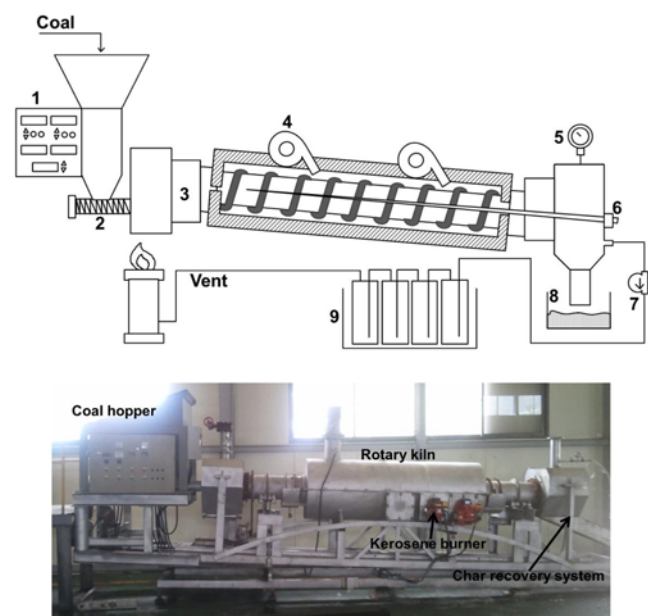


Fig. 2. Schematic diagram and image of the rotary kiln reactor.

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|------------------|--------------------|------------------|
| 1. Control panel | 4. Kerosene burner | 7. Pump |
| 2. Screw feeder | 5. Pressure gauge | 8. Char receiver |
| 3. Rotary kiln | 6. Thermocouple | 9. Tar trap |

devolatilization of BC with inherent moisture in the rotary kiln was tested with coal supplied at 15 kg/h. The rotation speed of the kiln was adjusted to give coal residence times of 30 minutes. The tar and moisture byproducts were removed by a cold trap, and the remaining dry gas was analyzed by gas chromatography.

RESULTS AND DISCUSSION

1. Analyses of Raw and Devolatilized Coal

The various coals with similarly sized particles were devolatilized at different temperatures and constant residence times. Proximate analyses of the char generated at 600–800 °C are listed along with the elemental analyses and fuel characteristics of that generated at 800 °C in Table 1. Most of the coal moisture was removed and the remaining volatile matter was inversely proportional to the temperature of devolatilization. The raw coals' high heating values were ranked BC>SOC>SOC-D, and high heating values of char devolatilized at 800 °C were ranked BC800>SOC-D800>SOC800. SOC-D800 had a higher ash content and a greater higher heating value than SOC800, because it contained more fixed carbon. Parikh et al. reported an empirical formula for easily predicting heating values via the proximate analysis of dry coal: $HHV = 0.3536FC + 0.1559VM - 0.0078ASH$ (MJ/kg). It shows that fixed carbon content affects HHV greater than volatile matter [15].

2. Devolatilization Rate and Char Yield

Proximate analysis (Table 1) allowed the calculation of the rates of devolatilization and char yields (Figs. 3 and 4). For all the coal types, the devolatilization rate was proportional to the temperature, while char yield behaved oppositely. Increased devolatilization rates generally contribute to reduced char yields. BC showed higher devolatilization rate than SOC and SOC-D at higher temperature and higher char yields overall because of its lower inherent moisture content than SOC. That means BC has higher carbon content, which can be converted to char as shown in Table 1. Mass loss in BC by the removal of volatile matter was greater than in SOC; however, mass loss in BC by the removal of inherent moisture was less than in SOC. Therefore, BC showed both higher char yields and higher devolatilization rates. SOC-D showed the highest devolatilization rate at

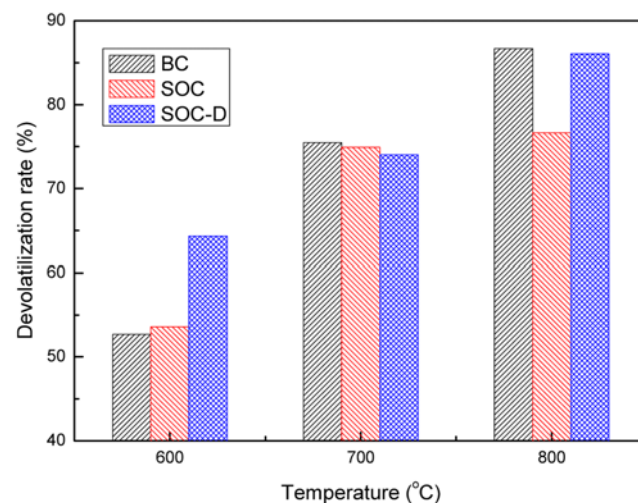


Fig. 3. Devolatilization rate with temperature.

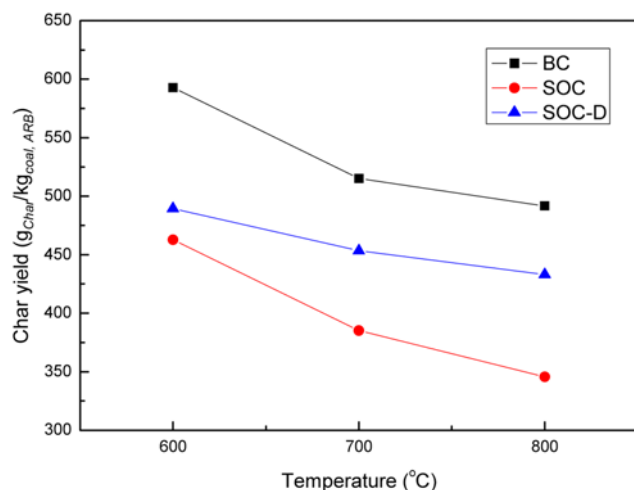


Fig. 4. Char yields with temperature.

low temperature. It showed a similar devolatilization rate to BC at high temperature. However, it showed lower char yields than BC because of its higher content of volatile matter, which arose due to its dehydration and led to large differences in the absolute amounts of removed volatile between it and BC. Each sample's rates of devolatilization and char yields were inversely proportional to each other; though the relationship was not consistent between the different coals because they each had different levels of inherent moisture, ash, fixed carbon, and volatile matter.

3. Tar Production

During devolatilization, the weaker bound components of the molecular structure break first and are discharged as tar. Therefore, the discharged tar is closely associated with the coal's structure and functional groups [16]. Tar production depended on the temperature of devolatilization, and tar compositions with a dominant concentration of light tar are shown in Table 3. At 600 °C, tar comprised toluene in light tar (boiling point, 110.6 °C). At 700 °C, five additional aromatic compounds were also detected, including polycyclic aromatic hydrocarbons, such as phenol and naphthalene, with higher boiling points (*ca.* 180 °C). The diversity of the aromatic tar compounds increased further with devolatilization at 800 °C, with polycyclic aromatic compounds containing three or more rings, such as dibenzofuran and fluorene (boiling points >285 °C), being detected.

Table 3. Tar composition from BC

BC600	BC700	BC800
Toluene	Benzene	Benzene
	Toluene	Cycloheptatriene
	Xylene isomers	Xylene isomers
	Phenol	Trimethylbenzene isomers
	Naphthalene	Hydroxyphenyl Phosphoric acid
		Phenylpropyne isomers
		Methylphenol isomers
		Naphthalene
		Dimethylbenzofuran isomers
		Bicycloundeca pentaene
		Dibenzofuran
		Fluorene

Table 4. Tar yields with temperature

Sample	Temperature (°C)	Tar yield (g _{tar} /kg _{coal, ARB})
BC	600	218.38
	700	208.98
	800	7.00
SOC	800	22.80
SOC-D	800	209.62

Devolatilization at lower temperatures generally produces organic compounds with lower boiling points, as did BC [13].

Tar yields varied with temperature (Table 4). They were measured by subtracting the mass of moisture and isopropanol from the total mass of liquid within the tar trap. BC produced less tar at higher temperatures, with production at 800 °C being substantially reduced. Tar yields were decreased with devolatilization temperature because of increase of reactivity between inherent moisture and volatile matter, which can be converted into tar, but its composition became more diverse. This suggests that the higher temperatures facilitated secondary pyrolysis that decomposed the tar into light gases such as hydrogen, carbon dioxide, methane, and carbon monoxide. This reduced the tar yield and increased the light gas yield [17]. Tar's conversion to light gas was caused by its decomposition and also by its gasification by steam and carbon dioxide. SOC-D showed substantially higher tar yields than SOC (Table 4). Steam generation by the dried SOC-D was presumably much less than by SOC, disabling tar to be converted into light gas through steam gasification; therefore more tar resulted.

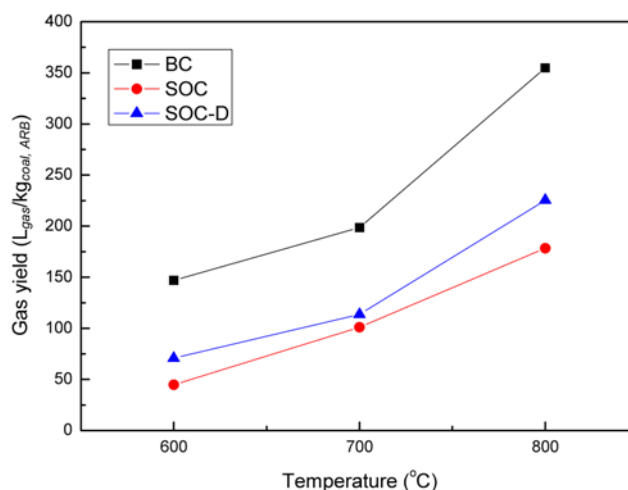


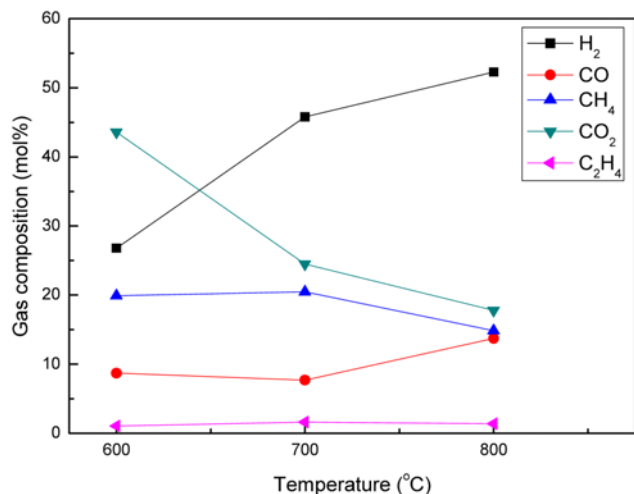
Fig. 5. Syngas production with temperature.

Table 5. Total product yields with temperature

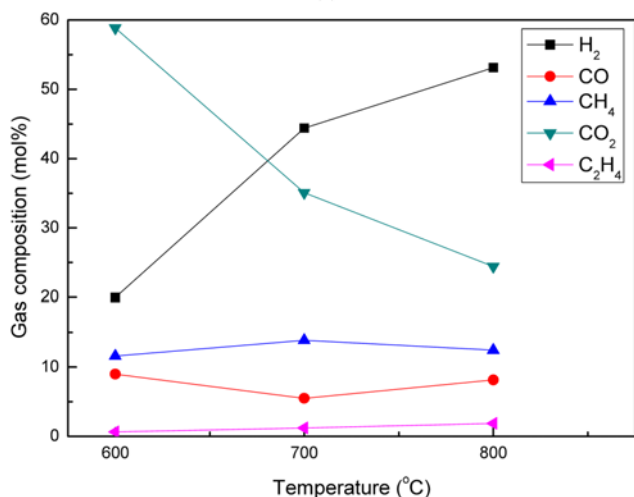
Sample	Temperature (°C)	Product (g/kg _{coal, ARB})		
		Gas	Char	Tar
BC	600	167.94	592.68	218.38
	700	155.72	515.15	208.98
	800	245.04	491.73	7.00
SOC	800	132.17	345.70	22.80
SOC-D	800	184.34	433.04	209.62

4. Gas Production

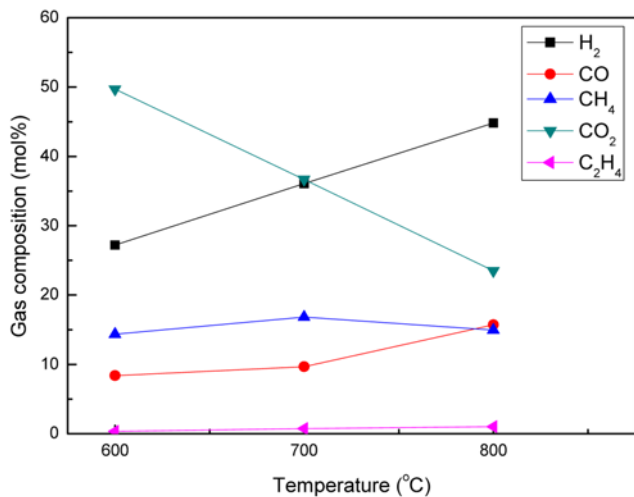
Coal gas discharged from each of the coal types increased with increasing devolatilization temperature (Fig. 5); the total products



(a)



(b)



(c)

Fig. 6. Composition of syngas from (a) BC (b) SOC (c) SOC-D in the fixed bed reactor.

from BC, SOC and SOC-D are shown in Table 5. Coal gas yields were ranked BC>SOC-D>SOC. BC yielded more coal gas than SOC mainly because of its higher devolatilization rate. However, SOC-D showed a similar devolatilization rate to BC but the lowest coal gas yield; its volatile matter was mostly converted into tar during pyrolysis.

The composition of the coal gas varied by coal type and devolatilization temperature (Fig. 6), depending on the decomposition reactions of the diverse functional groups in the coal, the gasification of steam or CO₂ in the fixed carbon and volatile matter, and the multiple gaseous reactions between the generated gaseous species. Hydrogen could be created by cleavage during the combination of C-H and O-H within the coal, the decomposition of tar, the steam gasification of char and tar, CO₂ gasification, the water gas shift reaction, and steam reforming in methane. Carbon monoxide has been reported to be generated by the decomposition of oxygen-containing groups such as hydroxyl, ether, or carbonyl and the steam or CO₂ gasification of char or tar. Carbon dioxide can be produced by the decomposition of monocarboxylic acid and the WGS reaction. Light hydrocarbons, such as methane and ethylene, can be generated by the decomposition of methoxy groups and aliphatic side chains. Acetylene is mostly produced by the decomposition of ethylene.

Hydrogen production increased and carbon dioxide production decreased with increasing reaction temperature (Fig. 6). The increase of hydrogen production was due to the decomposition of various functional groups, the steam gasification of char or volatile matter, and reforming reactions in the light hydrocarbon gas. Carbon dioxide production dropped as the exothermic WGS reaction was less favorable at higher temperatures. SOC produced more hydrogen than SOC-D, though it generated less methane and carbon monoxide, due to its inherent moisture increasing the activities of methane steam reforming and the WGS reaction. BC produced less carbon dioxide and more methane than SOC, contributing to the higher heating value of its coal gas. All the coals produced coal gas with less than 3% C₂ hydrocarbons, which can increase the heating value of coal gas. BC and SOC that retained their inherent moisture produced significantly higher amounts of hydrogen at higher temperature, suggesting that coal gas with hydrogen as its principal component was created under the high-temperature steam formed by the coal's inherent moisture. Coal devolatilization generally produces light hydrocarbons such as methane, rather than hydrogen, at the temperatures tested here. However, the coal gas generated here had hydrogen as its principal component.

Further characterization of the coal gas produced under steam was undertaken by devolatilizing coal in a rotary kiln that allowed the continuous generation of steam from the coal's inherent moisture, unlike in the fixed bed reactor. Coal gas with syngas as its principal component was created in a steam atmosphere at 700 and 800 °C (Table 6). At these temperatures, the concentrations of methane and

Table 6. Composition of syngas from BC in the rotary kiln

Temperature (°C)	Composition (mol%)				
	H ₂	Air	CO	CH ₄	CO ₂
700	42.27	3.50	17.81	16.48	19.95
800	52.65	2.02	34.42	5.26	5.65

carbon dioxide were significantly reduced, while those of hydrogen and carbon monoxide increased. This was likely due to the activation of steam gasification reactions of the char and tar and CO₂ gasification reactions at the higher temperatures. Methane and carbon dioxide concentrations dropped because of activation of the strongly endothermic CO₂ reforming reaction of methane.

Unlike in existing processes, in which coal gas is consumed as a thermal energy source, if coal gas with hydrogen or syngas as the principal component is produced from devolatilization, as was observed in the fixed bed reactor, it can be used in the high value-added fields such as synthetic petroleum or fuel cells. Furthermore, the low-temperature pyrolysis of coal at low pressure, unlike gasification, could simultaneously produce clean char and high value-added syngas for fuels with better thermal efficiency and lower carbon emissions.

CONCLUSIONS

The following conclusions were obtained through investigating devolatilization of Mongolian brown coals with the coal types, dry basis and the reaction conditions.

The raw coal samples showed higher heating values inversely proportional to their ash content. Char devolatilized at 800 °C showed HHVs that depended on their fixed carbon content, with SOC-D800 showing a higher HHV than SOC800 despite its higher ash content. All the coals showed increased devolatilization rates and lower char yields with increasing temperature. While higher devolatilization rates generally reduce char yields, BC showed both higher devolatilization rates and char yields than SOC and SOC-D. This was attributable to mass loss in BC by the removal of volatile matter being greater than in SOC, but its mass loss by the removal of inherent moisture was smaller than in SOC. SOC-D showed lower char yields than BC despite its similar devolatilization rate at high temperature because its content of volatile matter was increased due to its dehydration. Therefore, even its similar devolatilization rate could not affect the absolute amount of removed volatile matter. Tar yields decreased with increasing temperature, but the tar produced contained more diverse components with higher boiling points. Coal gas produced at high temperature from the samples that retained their inherent moisture contained considerably higher amounts of hydrogen than that from the dried coal, indicating that hydrogen was created in the high-temperature steam atmosphere

that from the coal's inherent moisture. The formation of coal gas under steam was further investigated by conducting devolatilization in a rotary kiln that could continually provide steam from the coal's inherent moisture, unlike in the fixed bed reactor. Coal gas with syngas as the main component was created at 700 and 800 °C under the steam atmosphere. This paper contains information of devolatilization characteristics of Mongolian coal and suggests that the process with inherent moisture could produce not only improved syngas composition but also clean char simultaneously during coal devolatilization.

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