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Integrated process of coal pyrolysis with CO_2 reforming of methane by spark discharge plasma

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ABSTRACT

An integrated process of coal pyrolysis with CO_2 reforming of methane by spark discharge plasma was developed to improve the tar yield of coal pyrolysis. The effects of the reactor configuration parameters and the integrated process conditions were investigated. It was found that the conversions of CH_4 and CO_2 and the selectivies of H_2 and CO increase with the discharge input power. The electrode with a large- diameter and long discharge gap are unbeneficial to conversion of CO_2 and CH_4. The reaction temperature has little effect on the conversion of reaction gases. In the integrated process, the tar and water yields increase with the pyrolysis temperature and holding time. The pyrolysis atmosphere remarkably influences the tar yield. Compared with the pyrolysis under N_2 (Py-N_2) or the mixture gas of CO_2 and CH_4 (Py-MG), the integrated process of CO_2 reforming of CH_4 with coal pyrolysis can produce more tar, which is ascribed to the interaction of activated CH_4 by spark discharge plasma with the free radicals from coal pyrolysis. The tar yield is 1.4 times as Py-MG, and 1.5 times as Py-N_2 at the pyrolysis temperature of 550 °C.

1. Introduction

Coal tar, as a complex mixture of aliphatic hydrocarbons, phenols and aromatics, is an alternative feedstock to produce transportation fuels and important resource of chemicals, especially some high-added value polycyclic and heterocyclic aromatic hydrocarbons, which are difficultly derived from petroleum [1,2]. Therefore, increasing tar yield in coal pyrolysis is an effective approach to improve the economics of pyrolysis process.

Various methods were taken to improve tar yield, including coal pretreatment [3–6], catalytic pyrolysis [7–9], pyrolysis under different atmospheres [10–13], etc. According to the pyrolysis mechanism proposed by Liu [14], a large number of free radicals with different molecular sizes will be produced via the cleavage of weak covalent bonds at certain temperature. Tar is formed when the appropriate free radicals are stabilized. Coal tar may suffer secondary reactions, e.g., polymerization and/or decomposition, to form char or gas products at high temperature and/or long resident time, which suggests that the potential solutions to improve tar yield should produce more free radicals from coal cracking, effectively stabilize the resultant free radicals and avoid secondary reactions. Therefore, some researchers expected to adjust free radicals through coal pretreatment before pyrolysis or changing the pyrolysis temperature [15–17]. Lei et al. [16,17] found that tar yield, especially oil fraction drastically increases after pretreatment of Shengli lignite with ionic liquid, and believed that the composition changes of oxygen-containing functional groups in coal contribute to improvement of tar yield. Wang et al. [18] upgraded Inner Mongolia lignite by hydrothermal treatment before pyrolysis and found tar yield raised about 18%, and ascribed to the increasing free radicals in the treated coal. Li et al. [19] used Ni/MgO-Al_2O_3 to in-situ upgrade the high temperature pyrolysis vapor derived from coal pyrolysis and obtain high tar yield.

Our previous studies showed that tar yield was remarkably improved by an integrated process to couple coal pyrolysis with catalytic activation of CH_4, such as CO_2/steam reforming of CH_4 [20,21], methane aromatization [22]. For example, tar yield can be increased by 80% at 750 °C in the integrated process compared to that under N_2 atmosphere [20], which is ascribed to the interaction of free radicals formed from CO_2 reforming of methane (CRM) with those from the cracking of coal structure in pyrolysis [23]. Catalytic CRM is usually carried out at the temperature of above 700 °C, higher than the optional temperatures (500–650 °C) of coal pyrolysis with high tar yield. To

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solve the temperature mismatching, He et al. [24] utilized dielectric barrier discharge plasma to activate methane and integrated it with coal pyrolysis. The results showed that tar yield was about 2 times as that under N_2 at low temperature of 400 °C. High tar yield is attributed to the participation of the active species from mixture gas plasma into the tar formation.

Compared with other non-thermal plasmas, spark discharge plasma (SPD) with the advantages of high density, high discharge channel temperature, high reactant conversion and low energy consumption is an effective approach to activate CO_2 and CH_4 to syngas production [25]. Zhu's work [25–27] showed that the spark discharge with kilohertz frequency exhibited excellent performance for CRM. The lowest energy cost and highest fuel-production efficiency at high reactant conversions can be achieved in comparison with other non-thermal discharge technique. Therefore, in this work, methane was activated by spark discharge plasma and coupled with coal pyrolysis to improve tar yield.

2. Experimental

2.1. Coal sample

A Chinese Buliangou subbituminous coal was crushed, sieved to 20–40 mesh and dried under vacuum at 65 °C for 10 h. The proximate and ultimate analyses are given in Table 1.

2.2. Apparatus and procedures

Fig. 1 illustrates the schematic diagram of the experimental setup. CO_2 reforming of CH_4 by SDP and its integrated process with coal pyrolysis was carried out in a quartz-tube reactor with an inner diameter of 21 mm shown in Fig. 2. The SDP reactor mainly consists of a stainless steel tube as the high-voltage electrode and stainless steel rod as the ground electrode. Considering the integrated process of coal pyrolysis with CRM and adjustable discharge gap, the two electrodes were vertically and coaxially fixed into the cylinders and sealed, respectively. This specially designed reactor structure (Fig. 2) can avoid the condensation of pyrolysis tar on the electrodes and unstable discharge caused by the deposit of coal tar. The plasma generator (CTP–2000 K, Nanjing Suman Electronics Corp.) was used to provide a sine wave voltage with the maximum voltage of 40 kV and an adjustable frequency between 10 and 40 kHz. The high-voltage was monitored and measured by a Tektrnix 2022 B digital storage oscilloscope sampling at 200 MHz. The discharge power was calculated according to the ref. [24].

Before the experiment, about 5 g coal sample was put downstream of the discharge zone so that the activated gases by the discharge can react with the free radicals from coal pyrolysis. After the system was purged by high-purity N_2, the mixture gas of CO_2, CH_4 and N_2 with a total flow rate of 200 ml/min, controlled by mass flow controllers, was introduced into the reactor through the high-voltage electrode at room temperature as the feed gas. Then the gas charge was initiated and the reactor was loaded into the center of the preheated furnace with the designed temperature. The reactor was heated from room temperature to the desired temperature within 10 min, and held for a desired pyrolysis time. A thermocouple attached to the outer wall of the quartz reactor at the center of the coal bed was used to monitor the pyrolysis temperature.

CO_2 reforming of CH_4 by the spark discharge plasma was carried out as same as the integrated process except without coal loading in the reactor.

Table 1
Proximate and ultimate analyses of Buliangou coal.

Proximate analysis (wt.%)			Ultimate analysis (wt.%, daf)				
M_{ad}	A_d	V_{daf}	C	H	N	S	O*
3.01	14.73	31.49	82.22	5.16	1.53	0.60	10.49

* By difference.

2.3. Conversion, selectivity and products yield

The pyrolysis liquid products including tar and water were collected in a cold trap at −20 °C. The pyrolysis water amount is determined according to the ASTM D95-05^{e1} (2005) method using toluene as solvent. The gas products were analyzed by GC7890II equipped with a thermal conductivity detector (5A molecular sieve packed column) and a flame ionization detector (GDX502 packed column). As to the CO_2 reforming of CH_4 by the SDP without coal pyrolysis, the gas products were collected for analysis after the stable discharge of 10 min. For the integrated process, all the gases were collected for analysis. N_2 in the feed gas was used as the internal standard gas to calculate the conversions of CH_4 and CO_2.

The conversions of CH_4 and CO_2, the selectivities of H_2, CO and C_2H_2 were calculated according to the Formulas (1)–(5). Tar and char yields were calculated by the Formulas (6) and (7).

$$X_{CH_4} = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100\% \quad (1)$$

$$X_{CO_2} = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \times 100\% \quad (2)$$

$$S_{CO} = \frac{F_{CO,out}}{X_{CH_4} \times F_{CH_4,in} + X_{CO_2} \times F_{CO_2,in}} \times 100\% \quad (3)$$

$$S_{H_2} = \frac{0.5 \times F_{H_2,out}}{X_{CH_4} \times F_{CH_4,in}} \times 100\% \quad (4)$$

$$S_{C_2H_2} = \frac{0.5 \times F_{C_2H_2,out}}{X_{CH_4} \times F_{CH_4,in} + X_{CO_2} \times F_{CO_2,in}} \times 100\% \quad (5)$$

$$Y_{tar} = \frac{W_{tar}}{W_0 \times (1 - A_{ad} - M_{ad})} \times 100\% \quad (6)$$

$$Y_{char} = \frac{W_{char} - W_0 \times A_{ad}}{W_0 \times (1 - A_{ad} - M_{ad})} \times 100\% \quad (7)$$

where, X and S represent the conversion of feed gases and the selectivity of the products; $F_{CH_4,in}$ and $F_{CO_2,in}$ refer to the flow rates of CH_4 and CO_2 in the inlet (ml/min), respectively; $F_{CH_4,out}$, $F_{CO_2,out}$, $F_{H_2,out}$, $F_{CO,out}$ and $F_{C_2H_2,out}$ are the flow rates in the effluent gas (ml/min), respectively. W_o is the weight of coal (g); W_{tar} and W_{char} are the weight of tar and char obtained during pyrolysis (g). A_{ad} and M_{ad} are ash and moisture content of coal sample on an air-dried basis (wt.%).

2.4. TG-DTG analysis of coal sample

Coal pyrolysis behavior was investigated using a Mettler Toledo TGA/SDTA851^e thermogravimetry analyzer. About 15 mg coal sample was placed in a ceramic crucible and heated from 25 °C to 850 °C with a heating rate of 10 °C/min using N_2 as the carrier gas at a constant flow rate of 60 ml/min.

3. Results and discussion

3.1. CO_2 reforming of CH_4 by SDP

3.1.1. Effect of input power on CO_2 reforming of CH_4

Fig. 3 illustrates the effect of input power on the reactant conversion, product selectivity and H_2/CO ratio while maintaining the constant feed gas rate at 200 ml/min and discharge distance of 8 mm. As shown in Fig. 3a, high input power obviously enhances the conversion