THE CHARACTERISTICS OF SEMI-COKES—THE SOLID RESIDUES FROM COAL PARTIAL GASIFICATION

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Abstract: In this paper the proximate analysis and ultimate analysis of sulfur in different semi-cokes generated from Rizhao bituminous coal and Beijing anthracite under different temperatures is done. Also the tendency of the contents of volatile, ash, fixed carbon and sulfur in different semi-cokes along with the different preparation temperatures is studied. Then the combustion experiment of semi-cokes in the drop-tube furnace system was carried out, and the kinetic parameters of different semi-cokes ware calculated.

Keywords: partial gasification, semi-cokes, combustion, kinetic parameters

INTRODUCTION

In China, the amount of production and consumption of coal is very enormous. Coal is the primary resource in Chinese energy system for a long time in the predictable future. But in China today, the mayor way to utilize coal is burning coal to generate electricity, which brings many serious problems, such as lower energy converting efficiency, higher air pollution, etc. In order to improve the energy utilizing efficiency and protect the environment, the alternative way to utilize coal is proposed. So China began to advocate Clean Coal Technology from 1990s, and gasification technology is one of the most important technologies. It has the advantages of higher efficiency, lower pollution, so it has attracted many researchers. But the existing and conventional gasification technologies have common disadvantages: they often need the condition of higher temperature and higher pressure to convert the fixed carbon in coals into gaseous Hydrocarbon, which makes the gasification technology more complex and more expensive.

Recently, partial gasification technology was advocated. According to the different reactive characteristics of different constituents in coals, partial gasification technology utilizes the coal in different ways: the volatile is extracted to generate gas under lower temperature as gaseous/liquid fuel or chemical materials; and the solid residues which is so called semi-cokes are mainly used as fuel in combustion chamber to generate other form of thermal energy. This can improve the energy utilization efficiency and improve the environment. As the solid residues of partial gasification of coal, semi-coke has the property of high content of fixed carbon and ash, low content of volatile and low heat value, so it is very difficult to be burned in common combustion chamber. At present, the technologies to utilize semi-cokes are not satisfactory enough[1-5], so developing new method and technology to utilize semi-cokes is important. The research on partial gasification technology has been listed into "National Key Fundamental Research Program".

In this paper, two typical bituminous coal and anthracite (Rizhao bituminous coal and Beijing anthracite) were selected to generate different semi-cokes under different temperatures, and made accurate proximate analysis and ultimate analysis of sulfur element. Then the semi-cokes were burned in a fluidized bed reactor, and the kinetic parameters of different semi-cokes, the activation energy, E and the frequency factor, $k_{0,ch}$ were obtained.

COAL SAMPLES AND SEMI-COKES

Coal Analysis

The Rizhao bituminous coal and Beijing anthracite were selected to prepare semi-cokes, the proximate analysis and ultimate analysis of coal samples are listed in table 1.

Table 1 The proximate analysis and ultimate analysis data of the coal samples

Coal Samples	Proximate analysis (%)			Ultimate analysis (%)				
	A_{ar}	M_{ar}	V_{ar}	C_{ar}	H_{ar}	O_{ar}	N_{ar}	S_{ar}
Rizhao bituminous coal	27.00	0.42	18.19	62.01	2.86	5.28	0.94	1.79
Beijing anthracite	22.64	0.79	6.71	71.99	0.73	3.05	0.08	0.23

The coals are heated for a certain time under the temperature of 550℃、600℃、650℃、700℃ under the air-isolated conditions in a electric oven to generate the semi-cokes used in the experiment. The heating time is about 30 minutes. The same procedure was repeated three times and then averaging the data obtained to get a type of semi-coke.

The Proximate Analysis of Semi-Cokes

The different semi-cokes prepared under different temperatures, proximate analysis and ultimate analysis of sulfur element of semi-cokes were done accurately. The proximate analysis data of different semi-cokes is shown in table 2.

The relationship between the contents of volatile, ash and fixed carbon in different semi-cokes and the preparation temperature is shown in Figure 1, 2 and 3 respectively.

From Figure 1(a), 2(a) and 3(a) it can be found that the content of volatile in semi-cokes decreases with the increasing of the preparation temperature for semi-cokes from different kind of coals. Especially to the bituminous coal, the content of volatile decreases quickly from 18.19% of coal to 8.21% under 700 ℃, and it shows that most of the volatile releases into gas. The content of ash and fixed carbon has the increasing tendency. The absolute contents shown in Figure 1 (b), 2(b) and 3(b) mean the percentages of the mass of certain constituents in semi-coke divided by original mass of coal, from which semi-coke was made. From the figures it is found that with increasing preparation temperatures, the absolute content of volatile also drops quickly, while the absolute content of ash keeps almost constant. Since the ash does not take part in chemical reaction in semi-coke preparation, so for certain mass of coal, the absolute mass of ash will not be changed. The absolute content of fixed carbon drops little and it is assumed that little fixed carbon is oxidized during the preparation procedure since the Oxygen isolation is not perfectly in the oven.

Table 2 The proximate analysis date of different semi-cokes

The semi-cokes		C_{ad}(%)	W_{ad}(%)	A_{ad}(%)	V_{ad}(%)
Rizhao bituminous coal	550℃	68.13	0.36	21.57	9.94
	600℃	68.32	0.24	22.01	9.43
	650℃	68.86	0.19	22.03	8.72
	700℃	69.16	0.12	22.50	8.21
Beijing anthracite	550℃	70.27	0.22	24.59	4.92
	600℃	70.41	0.09	24.90	4.61
	650℃	70.85	0.06	25.11	3.98
	700℃	71.36	0.02	25.58	3.03

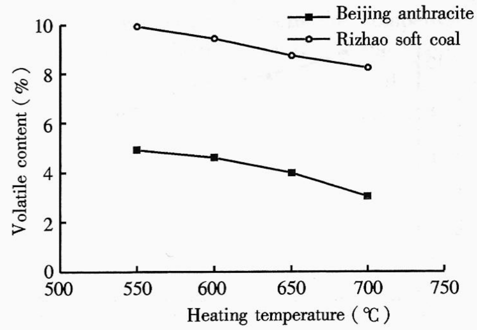


Figure 1 (a) Volatile content

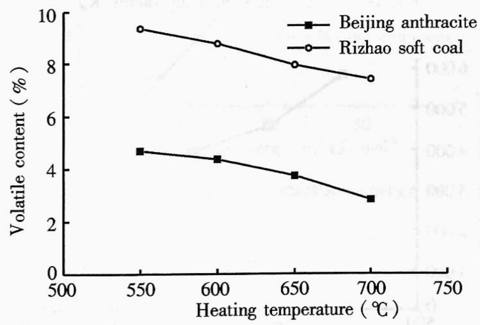


Figure 1 (b) Absolute volatile content

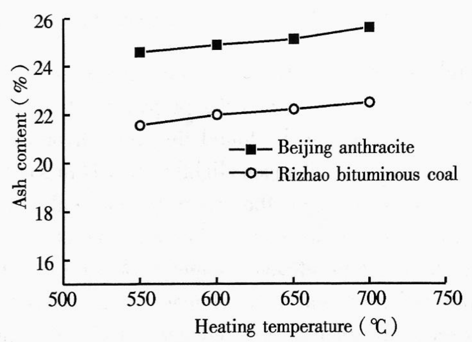


Figure 2 (a) Ash content

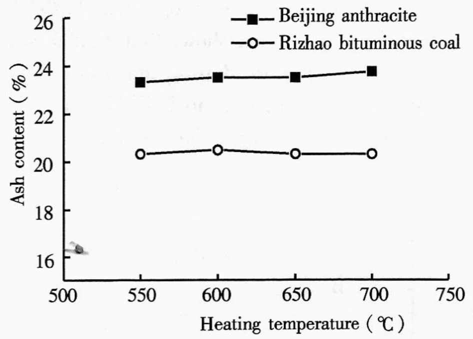


Figure 2 (b) Absolute ash content

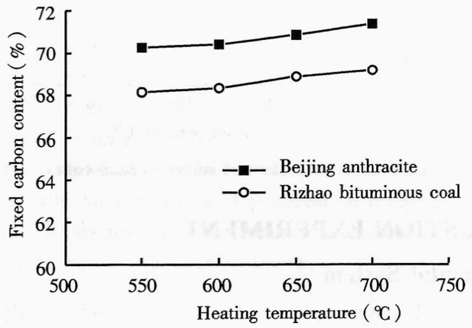


Figure 3 (a) Fixed carbon content

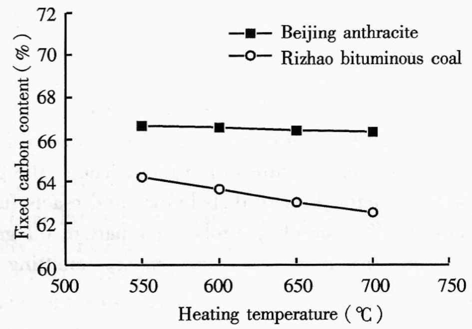


Figure 3 (b) Absolute fixed carbon content

The Ultimate Analysis of Semi-Cokes for Sulfur

The relationship of the sulfur content in different semi-cokes and the preparation temperatures is shown as Figure 4.

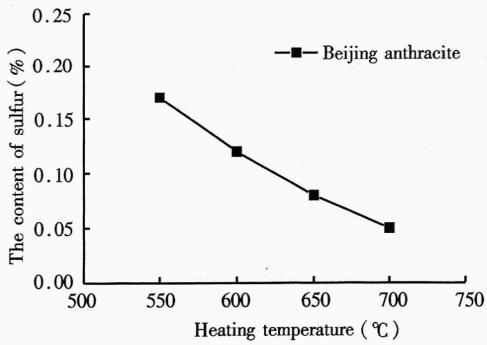


Figure 4 (a) Content of sulfur in semi-cokes

From Figure 4, it can be found that the content of sulfur in semi-cokes from different coals drops along with the increasing of preparation temperature. But for Rizhao bituminous coal, the sulfur content drops from 1.79% of coal to 1.00% under 700 ℃, and it shows that most of sulfur still keeps in semi-cokes, while to Beijing anthracite, the sulfur content drops from 0.22% of coal to 0.05% under 700 ℃, and it shows that most of sulfur has escaped into gaseous volatiles.

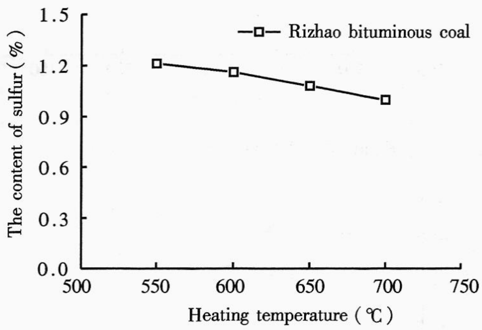


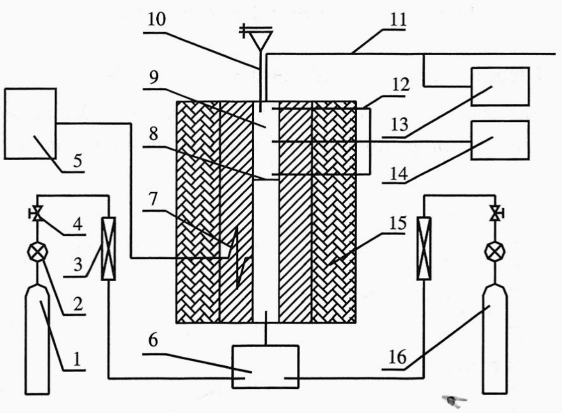
Figure 4 (b) Content of sulfur in semi-cokes

COMBUSTION EXPERIMENT

Experimental System

The combustion experiment was carried out in a drop-tube furnace system, which is schematically shown in Figure 5.

The experimental procedure is described as follows: the oxygen and nitrogen from gas cylinder get pass through the reductor, cut-off valve, flowmeter and then are mixed in the mixing region with certain proportion (O_2 21% and N_2 79% in volume in this experiment), and the mixed gas comes into the heating region from the bottom of the reactor, where it is heated up to the designed temperature in advance. Then, the gas goes into the bed of reactor through distributor, and reacts fully with the semi-cokes. The sampling probes get part of off gas; and the rest of off gas flows into the stack, emitting to the atmosphere.



1. Gas cylinder (N_2) 2. Reductor 3. Flowmeter 4. Cut-off valve 5. Voltage regulator 6. Mixing region 7. Built-in heater 8. Air distributor 9. Reactor 10. Chute 11. Flue gas 12. Thermal couples 13. Sampling probes 14. Computer 15. Thermal isolator 16. Gas cylinder (O_2)

Figure 5 The scheme of experimental system

The feeding rate of semi-cokes is 1.875 g (pure carbon)/min, and the flow rate of air is 2.0 m^3/h. The temperature in the reactor is selected 650 ℃, 700 ℃, 750 ℃, 800 ℃ respectively.

THE RESULTS AND DISCUSSIONS

The calculation of kinetic parameters in this paper is based on[6] and the Arrhenius Law. The activation energy E and the frequency factor K_0 of different semi-cokes are shown in Figure 6 and 7 respectively.

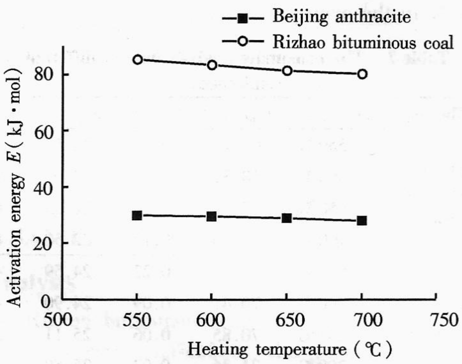


Figure 6 The activation energy E of different semi-cokes

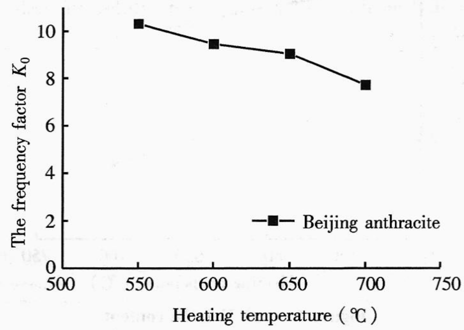


Figure 7 (a) The frequency factor K_0

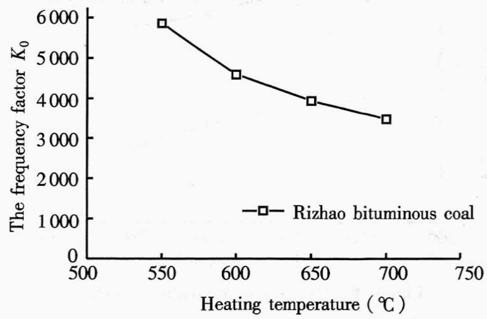


Figure 7 (b) The frequency factor K_0

The relation between the activation energy of semi-cokes under different temperatures and the preparation temperature is shown in Figure 6. It can be found that the activation energy from the same coal type changes slightly, that is to say that the energy needed to change the common molecule into the activation molecule in the combustion reaction of semi-cokes from the same coal type changes slightly. While the activation energy from different coal type changes greatly, that is the energy needed to change the common molecule into the activation molecule in the combustion reaction of semi-cokes from different coal type changes greatly. It is shown that the activation energy of semi-cokes depends on the coal type. That is also to say the physical and chemical characteristics of semi-cokes are very different from those of the coal char, so more experiment is important to study the combustion characteristics of semi-cokes.

The relation between the frequency factor of semi-cokes under different temperature and the preparation temperature is shown in Figure 7. It is found that the frequency factor of semi-cokes from different coal type changes greatly. Even to the semi-cokes from the same coal type, its frequency factor also changes along with the preparation temperature. But from the figure, it is found that the common changing tendency of the frequency factor of semi-cokes from the same coal is decreasing gradually along with the increasing of the preparation temperature. The reason of this phenomenon is the frequency factor is relative not only to the coal but also to the factor of the combustion state and the combustion condition, etc.

The relationships between the activation energy and the frequency factor of different semi-cokes are shown in Figure 8. From the figure it is found that along with the increasing of the activation energy, its corresponding ln K_0 increases in approximate line, which agrees with the compensation effect between the reaction activation energy and the frequency factor that Hashimoto[7], Fu[8, 9] have observed in their experiment. That means the frequency factor always increases along with the increasing of the reaction activation energy.

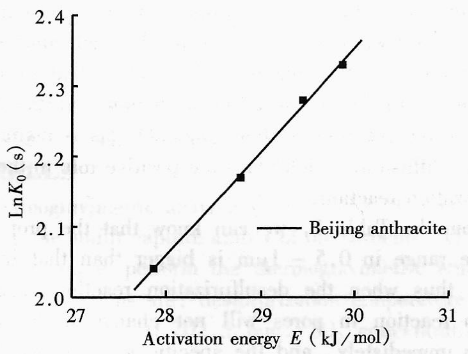


Figure 8 (a) Relationship between activation energy and frequency factor

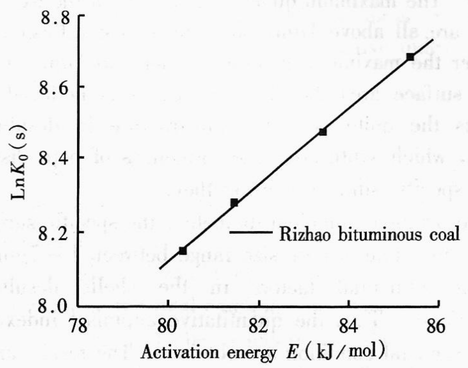


Figure 8 (b) Relationship between activation energy and frequency factor

CONCLUSIONS

(1) With the increase of preparation temperature, the content of volatile in semi-cokes from different kind of coals drops quickly, while the content of ash and fixed carbon increases slightly.

(2) Along with the increasing of preparation temperature, the content of sulfur in semi-cokes from different kind of coals has the decreasing tendency. But for Rizhao bituminous coal, most of sulfur still retains in the semi-cokes, while for Beijing anthracite, most of sulfur has escaped into gaseous volatiles.

(3) The activation energy of semi-cokes from different kind of coals is different greatly, while the activation energy of semi-cokes from the same type coal has little difference even for different preparation temperatures. It shows that the activation energy is dependent on the coal type.

(4) The frequency factor of semi-cokes from different kind of coals changes sharply, while the frequency factor of semi-cokes from the same kind coal has the decreasing tendency with the increasing of preparation temperature.

(5) The frequency factor always increases along with the increasing of reaction activation energy.

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