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Review of advance on coal pyrolysis mechanism

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ABSTRACT

Coal pyrolysis is a key technologies to clean coal utilization, which contributes to energy saving and environmental protection. This paper reviews the update findings of coal pyrolysis, which involves various factors. They affects the physical and chemical properties of coal char, coal gasification reactivity, and pyrolysis furnace structure. These findings show that inert atmosphere reduces the initial reactive char gasification. Hydrogen atmosphere increases chemical reactivity of coal char, methane atmosphere mixed with steam promotes the nitrogen emission. Pressurized pyrolysis makes C/H mole ratio of coal char increasing and the specific surface area decreasing, and limits volatiles separated out. Higher temperature is conducive to the coal char conversion, heating rate is helpful to the trace elements release and improves the reactivity of ash melting char. It found that temperature, pressure, and heating rate have mutual effects. In future studies, it is desirable to obtain coal char with high carbon content and excellent reactivity.

Keywords: Coal pyrolysis, Coal gasification, Retort furnace

INTRODUCTION

Coal clean application includes pyrolysis and gasification. Coal pyrolysis is the initial stage of coal gasification, and also the basis of the coal chemical processing. Pyrolysis conditions have a significant impact on coal tar yield and physicochemical properties, and also affects the coal char gasification reaction activity, such as coal char specific surface area, pore structure, carbon microcrystalline structure and so on. Pyrolysis conditions are mainly involved in temperature, heating rate, pressure and atmosphere. In recent years, a lot of research works has been carried out, including the analysis of coal pyrolysis factor and the improvement technique of the retort furnace.

1 Influential factor to coal Pyrolysis

The coal pyrolysis mainly adopts nitrogen, hydrogen, carbon dioxide and water vapor as the atmosphere. Because the secondary reaction of the coal char in inert atmosphere reduces the gasification reactivity of the coal char, Shenfu coal [1] char has higher gasification reactivity in hydrogen atmosphere than that in nitrogen atmosphere. At low temperature, methane and carbon dioxide had no significant effect on coal pyrolysis. However, at high temperature, methane reacts with organic matter in coal to produce aliphatic compounds, increasing the semi-coke yield. Carbon dioxide reacts with homo-aromatic, reducing the coal char yield. Methane atmosphere does not promote the change of N to NH_3, but adding small amount of steam promote production and release of NH_3. Thus, there is the synergistic role between methane and steam, which is the ability to promote NH_3 to form and release. Besides, the coal char yields obtained in methane atmosphere with 15% steam is half of the coal char in Ar atmosphere under the same conditions [2].

Pressure affects the release of volatile, swelling of coal particles and changes of coal structure. The current study pays more attention on bituminous coal with thermoplastic and lignite coal with high volatile and water contents. In pure nitrogen atmosphere, pyrolysis processing of both Fushun bituminous coal and Huangxie lignitous coal was observed at 0.1-0.6Mpa with PDTA [3], pyrolysis curves is divided into three stages: the coal desorption period is

200℃ ago, which deports physical water; coal pyrolysis period is 200-450℃, it appears an absorbed heat peak consistent with atmospheric pyrolysis curve; carbonization period is after 450℃, it appears an exothermic peak. Pressurized high temperature pyrolysis of both Fugu bituminous coal and Shengli lignitous coal was observed with TGA made in USA at 0.1-5Mpa[4]. With the increasing of pyrolysis pressure, C/H mole ratio obtained with two kinds of coal increases, the aromatic rate of coal tar increases, the order degree improves. The constraint role of the pressure improvement on the devolatilization mainly embodies in promoting the secondary reaction of the tar to produce the soot deposited on the surface of the coal char particles, increasing C/H mole ratio. In their experiments, adding pressure has more significant effect on lignitous coal than bituminous coal. They believed that adding pressure causes the polycondensation of the bituminous coal char and the release of more hydrogen, leading to the increasing of the C/H molar ratio. XRD patterns displayed that the old lignitous coal obtains the higher order degree of carbon compared to the younger under the same conditions. With the increasing of pyrolysis pressure, the amount of large pore in coal char increases, the amount of micropores reduces, the average pore radius increases.

High-pressure is not conducive to the release of the volatile component. With the increasing of pyrolysis pressure, hydrogen elements content in the solid coal particles significantly decreases. The higher pressure extends the residence time of the volatile in the solid char, in favor of volatiles secondary cracking. With the increasing of pressure, for quick gasification of coal char, 500℃ is the optimum pyrolysis temperature. For pressurized pyrolysis char particles, with the rise of the final pyrolysis temperature (500-800℃), gasification rate gradually increases, and then pyrolysis temperature continues to rise (about 1000℃), gasification rate decreases rapidly [5].

On the basis of the experimental data, Xiong [6] adopts the multiple linear regression to obtain the coal pyrolysis reaction kinetics mechanism equation, the average activation energy E and pre-exponential factor k . Although the reaction mechanism equation and kinetic parameters is an overall result, but has a certain practicality for simulation of complex chemical process.

Effects of temperature and pressure have mutual interaction. With the increasing of temperature, pressure affects the pyrolysis of coal particle significantly, and final temperature of pyrolysis also has an important effect on gasification activity. At 500-1000℃, an increase in the pyrolysis temperature is in favor of devolatilization, but char productivity reduces. As temperature increases, both pore surface area and volume of coal char increases firstly, and then decrease [7]. In addition, the char conversion increases with temperature at 1200-1400℃, the conversion time is shortened with the increase of temperature. As temperature ascends, the specific surface area of Shenfu slow pyrolysis char decreases. At higher temperature than 1100℃, Shenfu char melts and reunites into greater spherical particles. As for Shenfu fast char, specific area increases with pyrolysis temperature. At higher temperature than 1300℃, the minerals melts into small ball, slightly agglomerated trend. Shenfu slow pyrolysis char has larger graphitization degree than fast one [8]. At 1100-1600℃, 1-12bar pressure and inert atmosphere, coal broken degree increases with pyrolysis temperature, and changes with coal species[9].

As the heating rate increases, the initial pyrolysis temperature, and temperature at the loss weight peak and the final pyrolysis temperature migrates towards the high temperature zone, and DTG peak increases [10]. Coal char obtained at various pyrolysis rate appears various physical and chemical properties, due to the shorter resident time (<2s) of fast pyrolysis, hydrogen and nitrogen elements can't separate out in time. Therefore, fast pyrolysis char has a lower carbon content and higher Nitrogen and Oxygen contents than slow pyrolysis char. As the pyrolysis temperature increases, the specific surface area of slow pyrolysis char decreases, and that of fast pyrolysis char increases. Extremely fast pyrolysis conditions can make char pore more developed porosity, pore of coal char contains tar which is not completely precipitated, blocking coal tar partially pores, reducing the surface area of fast pyrolysis.

The heat absorption in the coal pyrolysis processing decreases as the heating rate increases. Coal pyrolysis produces tar components, including aromatic, cycloaliphatic and aliphatic. Their content is up to the maximum value, the corresponding highest pyrolysis temperature moves backwards as the heating rate increases, however, coal gas releases sharply[11].

Heating rate has a significant impact on Shenfu coal release of trace elements, the evaporation rate of trace elements increases as the heating rate and pyrolysis temperature (950-1300℃) increases [12]. Pyrolysis temperature at 950-1500℃, the ash melting pyrolysis char reactivity increases as the heating rate increases significantly, CO_2 gasification reactivity of coal char is controlled by diffusion process [13].

2 Gasification reaction kinetic properties

Coal gasification reaction kinetic properties are mainly controlled by diffusion and chemical reaction kinetic mechanism. Shenfu coal char relys on chemical reaction kinetic mechanism at 950-1150℃, and diffusion kinetics mechanism at 1150-1400℃ [14]. Mathematical model has been established based on the two mechanisms[15], it found that diffusion mechanism and coal particle radius affects the coal pyrolysis field [16]. Effect of steam on coal pyrolysis reduces with coal particle radius [17]. Coal pyrolysis rate is also controlled by internal and external heat transfer [18]. At higher temperature, coal pyrolysis rate relys on internal heat transfer. At low temperature, coal pyrolysis rate depends on external heat transfer. Weight loss during coal pyrolysis is caused by coal moisture, volatile matter, ash, fixed carbon, hydrogen, nitrogen and sulfur functions [19].

3 Pyrolysis devices of Yulin Shenfu Jurassic coal

Yulin Shenfu Jurassic coal has non-stick and weak-stick characteristics, the SH2007 type internal heat upright carbonization furnace was setted to retort Shenfu coal for yielding tar and coke. Heat carrier is applied to transfer heat to coal for thermal decomposition, generated raw coke oven gas is passed into the furnace to use again. It has many advantages, including continuous coking, large output, reasonable airflow and temperature distribution in furnace, etc. Besides, coke furnace works as a closed operation, which reduces the dust pollution and gas leaks. The whole sets of measurement and control technologies are applied to achieve automatic control on line, and recovery rate of coal tar is up to 15%. However, this process has stringent requirement to particle radius, which makes lots of pulverized coal ash difficult to be comprehensively utilized. In addition, heating media in the internal heating type of furnace mainly is air and gas, lots of raw coke oven gas can be applied because of low heat value. In order to prevent pulverized coal ash from polluting environment, pulverized coal is often made into block coal. Reference [21] provided block coal ratio to meet the pyrolysis strength. Block coal has an optimum strength at coal tar incorporation of 10%, raw water mass fraction of 13%, forming pressure of 63MPa. In order to improve the drawback of the existing furnace that only uses block coal as raw; a pulverized coal pyrolysis gasoline-electric muti-generation system is in research. The technology uses pulverized coal as raw material, and produces semi-char with medium-low temperature pyrolysis process and tar products, however, process and technology requires to breakthrough.

CONCLUSION

Currently, more researches focused on coal pyrolysis behavior at 850-1500℃. The relatives parameters includes temperature, atmosphere, heating rate, pressure. Moreover, the fixed sealed container is used to Pyrolysis process. Few works considers gas velocity effect on pyrolysis. Although the fixed sealed container has many advantages, such as safety, easy operation and monitor, it is far away from the actual production process. The obtained results only has qualitative guidance to the actual production process. Besides, coal pyrolysis is a complex physical and chemical processes coupled with gas-liquid-solid three-phase change, involving a large number of chemical reactions and intermediate products. So it is necessary to seek more practical experimental methods and establish reasonable mathematics model for optimizing the coke production process.

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