Desulfurization reaction model and experimental analysis of high sulfur coal under hydrogen atmosphere

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ABSTRACT

The reaction between hydrogen and high-sulfur coal at high temperature was investigated. Crashed and sieved high-sulfur coal sample was placed in a 23 mm I.D. differential reactor. The release of hydrogen sulfide at run temperature and under different hydrogen atmospheres was recorded by a hydrogen sulfide detector. Desulfurization yield was obtained through the elemental analysis of residual char. The grain reaction and random pore models were modified to facilitate the description of reaction kinetics characteristics. Hydrogen was observed to promote the desulfurization rate considerably; i.e., more than 65% of sulfur in coal could be removed. The releasing curves of H_2S in the hydropyrolysis process exhibited two peaks. The desulfurization process in the hydropyrolysis of high-sulfur coal could be regarded as two stages based on the evolution profiles of H_2S. The first peak at 250–450 °C was derived from the desulfurization of aliphatic sulfide. The second peak at 450–650 °C was produced from the sulfur in pyrite and aromatic thiophenic structure. The desulfurization of high sulfur could be described more effectively with the grain reaction model than with the random pore model. The random pore model was only adopted in the initial stage of sulfur removal of high-sulfur coal under hydrogen atmosphere. The grain reaction model was adequate for the entire stage.

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1. Introduction

China is the largest producer and consumer of coal in the world. In the future, coal will inevitably remain as the overwhelming indigenous energy resource. Thus, understanding the major trends and developments in this energy sector is essential in analyzing the current challenges that China is facing in terms of economy and environment. Coal accounts for more than 75% of the total commercial primary energy consumption in China. High-sulfur coal reserve makes up approximately 30% of total coal reserves. The proportion of high-sulfur coal mining has demonstrated an annual increase [1,2]. With the rapid development of the economy in China, severe environmental pollution has been generated as evidenced by the large amounts of SO_2 and NOx emissions resulting from coal consumption [3–6]. Pollution will not only result in the formation of photochemical smog and acid rain but will also have negative effects on human health. Moreover, pollution destroys the ecological environment and brings serious consequences on life and production [4–6]. According to the

projections for the next 50 years, the primary energy sources in China will remain coal based [1,6–10]. Thus, developing a low-cost, easy-to-operate coal desulfurization technology will have far-reaching economic and environmental significance.

Several desulfurization methods implemented before combustion have been proposed [1]. However, an economical and effective method for desulfurization has not been formulated yet. In addition to liquefied pyrolysis and gasification conversion, hydropyrolysis (Hypy) is the third conversion method which is highly regarded as a safe and clean alternative [10–15]. In this study, hydrogen pretreatment on the effect of coal pyrolysis desulfurization and the kinetics of sulfur removal from high-sulfur coal were investigated under hydrogen atmosphere at high temperature.
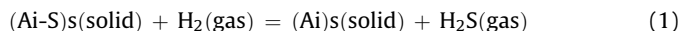
2. Desulfurization reaction model

Sulfur compounds in coal are divided into two categories: inorganic and organic sulfur. Inorganic sulfur is mainly pyrite sulfur and sulfate sulfur; whereas organic sulfur includes aliphatic sulfur, aromatic sulfur, and thiophene sulfur. The reaction of sulfur compounds during coal hydropyrolysis is complex. The results of this study were obtained using the first-order reaction model to

treat various parts of the experimental data with different conversion levels [15,16].

$$(Ai-S)s(solid) + H_2(gas) = (Ai)s(solid) + H_2S(gas) \tag{1}$$

The grain reaction and random pore models were used to define the mechanism of high-sulfur coal desulfurization by considering the structural characteristics of high-sulfur coal particles [15–18].

The results from the grain reaction model showed that the solid particles were composed of a large number of tiny crystals. The average diameter of the tiny crystals was approximately nm, and the particle size was 10^{-6} to 10^{-7} m. These crystals may be spherical, cylindrical, or sheets of non-porous materials. When these materials come in contact with gas reactants, the reaction could not be completed immediately. In addition, the particles could also be seen as a pile of ceramic aggregates that are closely held together. The gas diffusion in a small aggregate diameter was considered as a Knudsen type, which was significantly slower than the gas diffusion in the main hole. The materials were not absolutely non-porous, although they exhibited similar reaction behavior.

The reaction step of the gram model includes the gas reactant diffusion from the outer to inner surfaces, particle surface reaction, and reaction product gas diffusion from the inside to outside. According to the characteristics of the change in particle properties, a variety of gas–solid non-catalytic reaction models, which have a wide range of mathematical complexities, have been proposed. Among these models, the unreacted core and shrinking grain models are extensively applied. The shrinking grain model is applicable to solid particles that continuously decrease in size during reaction until they are consumed. During the reaction process, the outer layer of the particles is transformed into a solid or gaseous product. Size remains constant if the particle belongs to the unreacted core model. The core does not react, but the reaction interface is constantly advancing to the core. After a block of coal is ground, the pore structure of coal particles is destroyed. Coal particles consist of a large number of small spherical dense granules. After hydropyrolysis desulfurization, the particles remain unchanged. The gas–solid reactions on the outer surface and in the deeper layers of the solid particle do not take part in the reaction until the entire outer layer has reacted. The reaction zone gradually moves inward while constantly reducing the size of the core of unreacted solid and completely leaving the converted solid and inert material. The reaction of each particle is subjected to the unreacted core model. The continuity equation of a solid coal expressed by the unreacted core model of a single particle is as follows [19,20]:

$$\frac{\partial r_{gr}}{\partial t} = \frac{De_g r_{gc} k_s C_A}{De_g r_{gc} + k_s C_{sg}(1-(r_{gc}/r_{go}))} \tag{2}$$

where γ_{gc} is the unreacted core radius, m; C_A is gaseous reactant concentration, mol m^{-3}; C_{sg} is solid-phase reactants concentration, mol m^{-3}; De_g is the diffusion coefficient of gaseous reactants, m^2 s^{-1}; k_s is reaction rate constant, m^4 mol^{-1} s^{-1}; γ_{go} is the particle radius, m; t is time, s.

The boundary conditions can be expressed as

$$\gamma_{gc}\big|_{t=0} = \gamma_{go} \tag{3}$$

The conversion of a single particle can be expressed as

$$x_g = 1 - \left(\frac{r_{gc}}{r_{go}}\right)^3, \quad r_{gc} = r_{go}(1-x_g)^{1/3} \tag{4}$$

Simultaneously, $C_{Sg} = C_{So}(1-x_g)$,

$$\upsilon_S(\text{or } \upsilon_A) = -\frac{\partial C_s}{\partial t} = -C_{so}\frac{\partial(1-x_g)}{\partial t} = C_{so}\frac{\partial x_g}{\partial t}$$

where

$$\upsilon_S = \frac{3}{r_{go}} \cdot \frac{k_s C_A C_{Sg}(1-x_g)^{2/3}}{1+\delta_g^2[1-(1-x_g)^{1/3}](1-x_g)^{1/3}}$$
$$\frac{\partial x_g}{\partial t} = \frac{3}{r_{go}} \cdot \frac{k_s C_A(1-x_g)^{2/3}}{1+\delta_g^2[1-(1-x_g)^{1/3}](1-x_g)^{1/3}} \tag{5}$$

where $\delta_g^2 = k_s r_{go}/De_g$, which can be regarded as the modulus of the particle reaction. χ is the reaction fraction.

Assuming that the coal particle used has a uniform and fine size, and that the material layer is thin ($\delta_g^2 = 0$). The size of coal particle was fine, the internal mass transfer resistance of a single particle can be neglected. The reaction rate of the coal samples can be expressed as:

$$\frac{\partial x_g}{\partial t} = \frac{3k_s C_{Ago}}{r_{go}}(1-x_g)^{2/3} \tag{6}$$

Let be

$$\beta_1 = \frac{3k_s C_{Ago}}{r_{go}} \tag{7}$$

where

$$1-(1-x)^{1/3} = \beta_1 t \tag{8}$$

The random pore model assumes that finely grinding coal particles results in a porous structure. In this situation, the desulfurization reaction fulfills the assumptions of the random pore model. The desulfurization rate of a single particle can be expressed as:

$$\frac{dx}{dt} = k_o e^{-(E/R_r T)} g(P_{H_2}) f(x)(1-x)^n \tag{9}$$

In the experiment, $g(P_{H_2})$, $f(x)$ can be considered as constants. Let $n = 1$; thus, the integral equation can be expressed as:

$$\ln(1-x) = -\beta_2 t \tag{10}$$

where $\beta_2 = k_0 e^{-(E/R_r T)} g(P_{H_2}) f(x)$; E is the reaction activation energy, kJ mol^{-1}; R is gas constant.

The desulfurization reaction fulfills the assumptions of the grain model. The desulfurization conversion can be expressed by Eq. (10).

3. Experimental

The apparatus used in the study is shown in Fig. 1. The reactor was a stainless steel pipe mounted on a vertical tube furnace and controlled by the bed temperature. The gases produced were analyzed by gas chromatography (GC)-950 with a flame photometric detector. The gas intake was measured using a mass flow meter (Sevenstar D07-7B). Furthermore, the output of product gas flow was measured using a soap liquid meter [8–10].

The temperature of the reactor was increased with nitrogen purge. Hydrogen was introduced into the system at the start of the run. Adjustments were made to achieve the desired levels for the flow. After the run, the reactor gas was disassembled. The char produced was weighed and analyzed using a KZDL-3C sulfur determinator (Hebi Tainayuan Group) and VG Scientific ESCA-Lab220i-XL Electron Spectrometer for residual sulfur. All repeated experiments with large errors were rejected. The proximate and ultimate analysis of the coal sample was presented in Table 1.

The formula of desulfurization rate (SR) of coal was as followed:

$$SR\,(\%) = \frac{M \times S_0 - m \times s}{M \times S_0} \times 100$$