An operando analysis for gasification of carbonaceous material

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Highlights

- Char-Ash/Slag Transition during gasification was explored by operando analysis
- Two forms of char-ash/slag transition can well explain the variation of char reactivity
- A threshold value of gasification conversion (x = 0.9) exists during gasification

1. Introduction

Although there were many researches on the structure evolution in carbonaceous material gasification, most of the structure characterization was completed offline. After the reaction was completed, the sample was cooled to room temperature and collected to determine structure parameters. There were few studies on the in-situ structure evolution during high temperature pyrolysis and gasification. The high-temperature stage microscope system (HTSM) was used to investigate gasification of carbonaceous materials and showed novel advantages for studying char gasification characteristics [1, 2]. Therefore, it is worthwhile to combine HTSM, which can reveal gasification characteristic of single particle, with Raman spectroscopy to analyze the in-situ char gasification process. In this study, char gasification was carried out in HTSM to explore characteristics and mechanism of morphology evolution of char particle with carbon conversion. In addition, in-situ Raman spectroscopy was used to characterize in-situ evolution of carbon structure of single char particle.

2. Methods

Three coals with different ranks, i.e., Yunnan lignite coal (YN), Shenfu bituminous coal (SF), and Zunyi anthracitic coal (ZY) in China were chosen for experiments. The coals were crushed and sieved with an average diameter of ~120 μm. The in situ gasification experiments of char samples were carried out using a TS1500 heating stage microscope (Linkam Scientific Instruments, Surrey, UK). Detailed illustration of this experimental apparatus was presented in our previous study.27 The char samples were introduced into the holder of the heating unit at room temperature and were heated to the prescribed temperature (1000 or 1350 °C) in a continuous nitrogen flow of 100 $mL·min^{-1}$. The heating rate was set as 25 $°C·min^{-1}$. The temperature was controlled by the Linksys32 (Linkam Scientific) software package. After keeping in N_2 atmosphere for 5 min, the gas atmosphere was switched to CO_2 (100 $mL·min^{-1}$) for another 15 min at 1000 or 1350 °C to observe the interaction effects associated with char-ash/slag transition.

3. Results and discussion

The results show two reaction forms, which relate to the reaction conditions and coal properties in the char-ash/slag transition processes. (1) When the temperature was lower than the ash fusion temperature of coal, the char particles exhibited the shrinking particle mode in the initial and midterm reaction stages, and then showed the shrinking core mode at the late stage. The accumulated ash might block some pore structure of semicoke, which was unfavorable for the char-CO_2 reaction proceeding at high carbon conversions. (2) When the gasification reaction was conducted above the ash fusion temperature of coal, the liquid film formed because the ash melted with the shrinkage of char particles. Moreover, the molten slag enclosed residual carbon at high carbon conversions. There is a threshold conversion (x=0.9) during the evolution processes of lignite char samples to lignite slag/ash at 1200 °C and 1350 °C, while this threshold value is only existing at 1000 °C for rice straw char gasification.

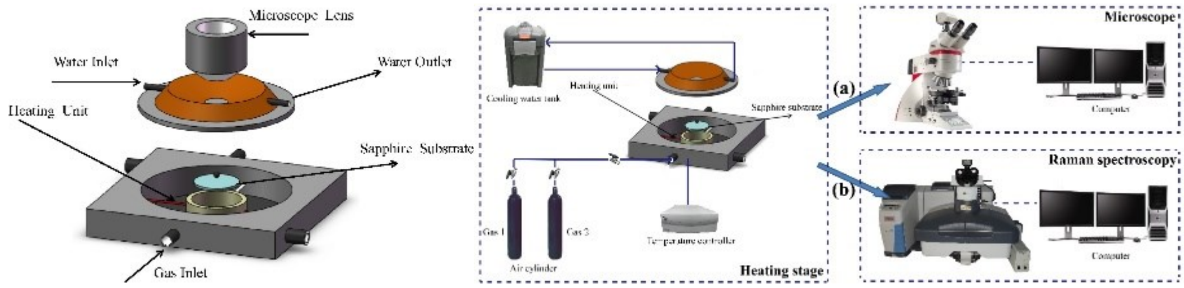

Figure 1. The schematic diagram of HTSM and operando Raman

The Morphology evolution of Lignite-raw-800P-1000G coal char and Lignite-de-ash-800P-1000G are shown in Fig. 2. The reaction of raw coal char is in the form of particle shrinkage in the first 3.6min, and then in the form of core shrinkage, while for de-ash coal char, follows particle shrinkage model for the whole stage .

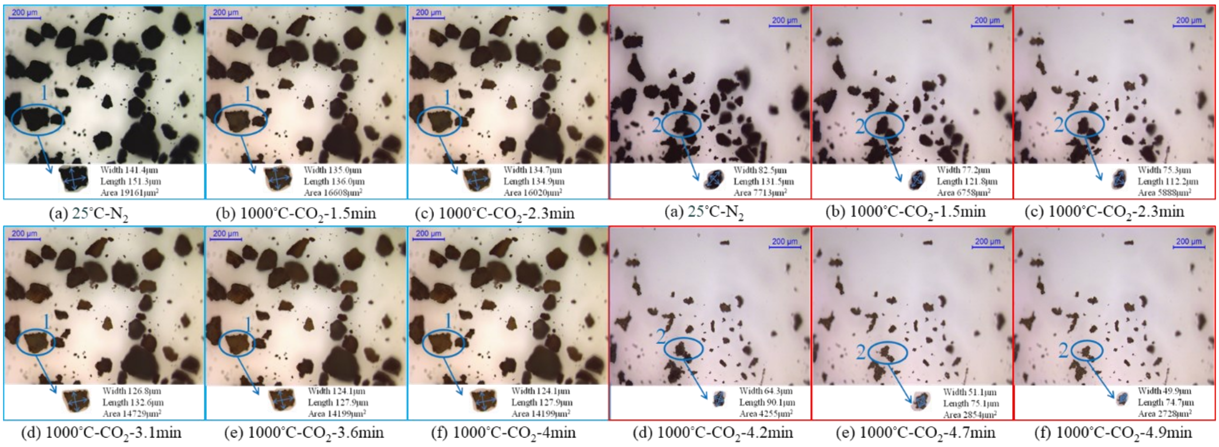

Figure 2. Morphology evolution of Lignite-raw-800P-1000G coal char and Lignite-de-ash-800P-1000G

4. Conclusions

When the reaction temperature was lower than the ash fusion temperature of coal, raw coal char particles shrank along with carbon conversion at the initial reaction stage. When the gasification reaction proceeded at high temperatures (above the ash fusion temperature of coal), the char particles shrinked and the liquid film formed due to the ash melt. In-situ Raman results showed that the catalytic effect of sodium-calcium binary catalyst was better than that of single catalyst, and gasification residue of binary catalyst loaded char had more calcium silicate and less sodium silicate than gasification residue of single-metal catalyst loaded char.

References

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Keywords

In-situ hot stage; gasification; carbon conversion; carbonaceous material