Fuel 163 (2016) 157–165

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

An experimental study of $CaSO_4$ decomposition during coal pyrolysis

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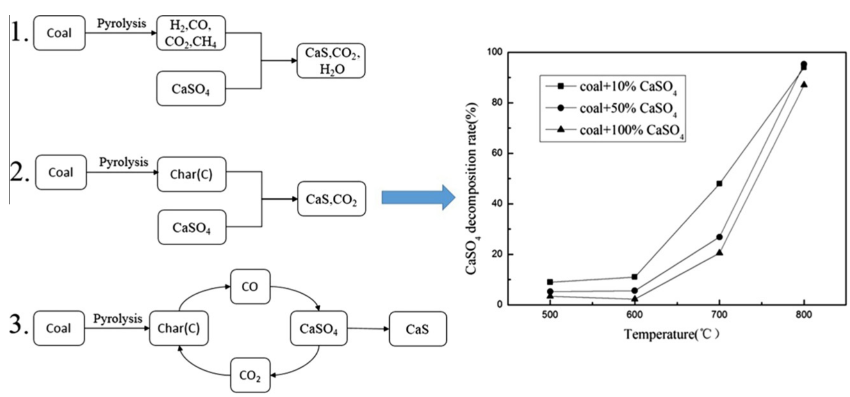
HIGHLIGHTS

- The coal strongly enhanced $CaSO_4$ decomposition during pyrolysis.
- The solid–solid reaction mechanisms could provide a better explanation for $CaSO_4$ decomposition during pyrolysis.
- The inherent minerals of coal could promote $CaSO_4$ decomposition.
- $CaSO_4$ decomposition rate was significantly decreased with the increase of coal particle size.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 June 2015
Received in revised form 21 September 2015
Accepted 22 September 2015
Available online 1 October 2015

Keywords:
Coal pyrolysis
$CaSO_4$ decomposition
Inherent minerals
Coal particle size

ABSTRACT

Coal with different proportions of $CaSO_4$ was pyrolyzed in a fixed-bed reactor in a temperature range of 500–800 °C to study the mechanism of $CaSO_4$ decomposition during coal pyrolysis. The results showed that the presence of coal could greatly promote $CaSO_4$ decomposition at high temperatures, and 87% $CaSO_4$ was decomposed at 800 °C during Xiaolongtan lignite pyrolysis, which was mainly attributed to the solid–solid reaction ($2C + CaSO_4 \rightarrow CaS + 2CO_2$). The effects of inherent minerals, coal type, holding time and coal particle size on $CaSO_4$ decomposition were also discussed. By comparing the $CaSO_4$ decomposition rate between raw coal and demineralized coal, it could be concluded that the inherent minerals could greatly enhance $CaSO_4$ decomposition at high temperatures, which was also be proved by the results of thermogravimetric analysis (TGA). $CaSO_4$ decomposition rate presented a significant decrease with the increase of coal particle size. Four coals used in this study could all promote $CaSO_4$ decomposition, but the promotion effect differed among those four coals which may be attributed to the difference in inherent minerals and the reactivity of coal.

1. Introduction

China has encountered serious oil shortage and severe environmental pollution in recent years, and it relies heavily on coal resource. However, the direct combustion of coal has relatively low thermal efficiency and gives rise to large amount of pollutant emissions. Based on this, the coal staged conversion process combined pyrolysis and combustion has been proposed [1]. Fig. 1 illustrates the principle of this process. In this process, coal is firstly fed to pyrolyzer for pyrolysis (500–800 °C), getting gas, oil and char. The heat for pyrolysis is provided by high-temperature circulating ash, which is separated in a cyclone and collected in the loop seal of a circulating fluidized bed (CFB) boiler. The pyrolyzed gas and oil are separated in the cyclone. Pyrolyzed gas and tar can be used for other purposes after cooling and purification. Pyrolyzed gas can

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http://dx.doi.org/10.1016/j.fuel.2015.09.054
0016-2361/

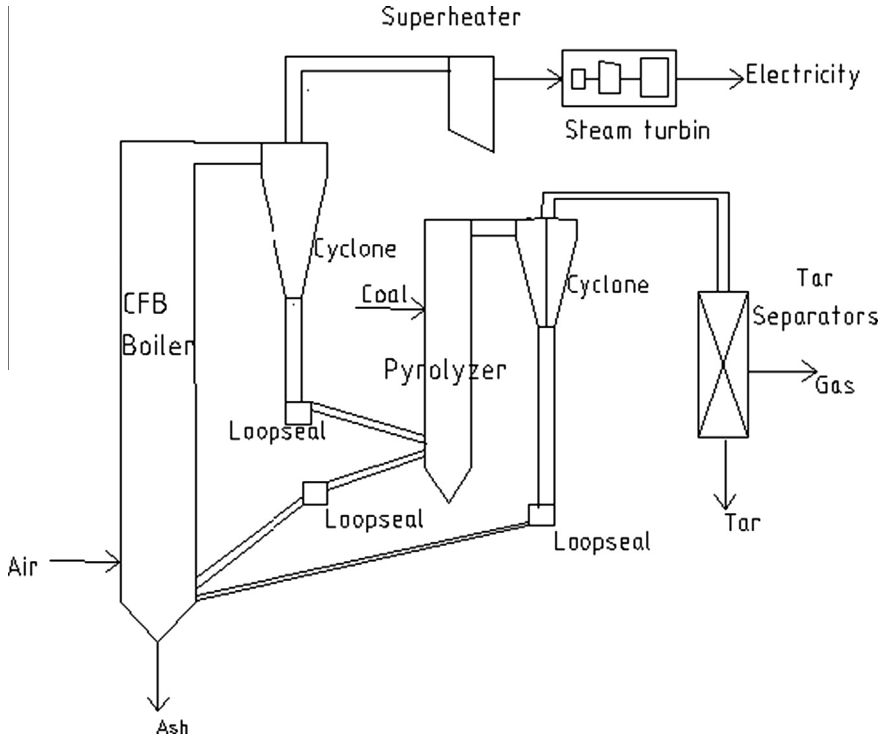

Fig. 1. The principle of the coal staged conversion process.

not only be used as domestic gas and gaseous fuel, but also be synthesised to liquid fuel after further clean-up. The tar can be applied to extract valuable products firstly, and then to be hydrogenated to oil. The char from the pyrolyzer is sent to boiler together with circulating ash and then burnt (800–1000 °C) for heat or electricity. The most outstanding characteristic of this process is that it can easily fulfill the coal staged conversion. In this process, the high valuable components of the coal can be extracted to get gas and oil during the pyrolysis and the other components are burnt in the boiler, whereas all components of coal are burnt in the direct combustion of coal, which leads to a waste of high valuable components of the coal. Therefore, the coal staged conversion process can significantly increase the value of comprehensive utilization of coal.

Due to the great prospect in coal utilization, a lot of experiments were carried out to study the characteristics of coal pyrolysis and combustion based on coal staged conversion process [2–4]. Guo et al. [5] analyzed economic feasibility of this process, finding that polygeneration plant based on the coal conversion process was more profitable than CFB power plant even when prices fluctuate within a wide range. The key technological problems of coal staged conversion process, such as circulating ash returning equipment, hot ash allocation and pyrolyzed gas cleanup, have been solved. Based on this, a pilot coal staged conversion process of a 75 t/h circulating fluidized bed (CFB) boiler combined with a moving bed coal pyrolyzer is designed and established [6]. The operation and test results of pilot plant show that the process is scaled up successfully from lab-scale to pilot plant. During the test, the stability of the coal staged conversion system is satisfactory and no operating problems are encountered. In addition, 1 MW bench scale facility and 12 MW, 40 t/h industry scale facilities based on the coal staged conversion process combined with coal CFB boiler with a fluidized bed pyrolyzer have been successfully established and continuously operated [7]. Operating results show that coal staged conversation system runs continuously and steadily, realizing poly-generation of heat, electricity, gas and tar from coal in one system and reducing NOx, SOx and other pollutant emission effectively.

The pyrolysis in the coal staged process is clearly distinguished from the traditional coal pyrolysis process by the interaction of coal and abundant circulating ash during the pyrolysis. Therefore, a complete understanding of the interaction of coal and circulating ash during the pyrolysis is necessary and some studies have been done. The yields of product were greatly affected by the temperature and the blending ratio of coal to hot carrier particles [3,8,9]. Qu et al. [10] investigated the sulfur transformation in the presence of circulating ash during coal pyrolysis, noticing that some gaseous sulfur was fixed by the coal ash. However, the mechanism of interaction of coal and coal ash during the process has not been fully understood due to the complex components of the circulating ash. The coal ash mainly consists of $CaSO_4$, Fe_2O_3 and SiO_2. $CaSO_4$ is one of the main reactive components in the ash [11] and may exert a great influence on coal pyrolysis. Thus the investigation about the interaction between coal and $CaSO_4$ can help us understand the mechanism of the interaction of coal ash and coal during the pyrolysis. But up to now, researches about $CaSO_4$ behavior during coal pyrolysis and the effects of $CaSO_4$ on coal pyrolysis were rarely seen. Therefore, a complete understanding of $CaSO_4$ behavior in the coal staged process is necessary.

Although $CaSO_4$ is one of the coal components, the content of $CaSO_4$ is usually rather low. Consequently, the studies of $CaSO_4$ behavior during the pyrolysis are rarely seen. However, the $CaSO_4$ content in the ash is usually much higher compared with that in the coal. This is because inherent or additional CaO could fix SO_2 from coal combustion and much $CaSO_4$ is produced in this process. In addition, to meet the pyrolysis temperature (500–800 °C), a great deal of high circulating ash is needed. The ratio of coal ash to coal usually ranges from 1 to 7. Therefore, the ratio of $CaSO_4$ to coal during the pyrolysis in the coal staged conversion process can be relatively high. So the aims of this paper are to give a comprehensive investigation of $CaSO_4$ (with high content) decomposition during coal pyrolysis and study the effects of the