Fuel 212 (2018) 268–273

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

The mineral evolution during coal washing and its effect on ash fusion characteristics of Shanxi high ash coals

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ARTICLE INFO

Keywords:
Shanxi high ash coals
Coal washing
Mineral evolution
Ash fusion characteristics

ABSTRACT

Gasification has been deemed as the most promising method for the thermochemical conversion of Shanxi high ash coals, although the use of these high ash coals leads to high consumption of coal and oxygen, low syngas yield and cold gas efficiency. In order to improve gasification efficiency, it is necessary to reduce the ash content of these Shanxi high ash coals. In this work, three representative Shanxi high ash coals were floated with $ZnCl_2$ flotation agent to obtain floated coal samples with different ash contents. The mineral evolution during coal washing and its effect on ash fusion characteristics were thoroughly investigated. A radio frequency oxygen plasma furnace, X-ray diffraction (XRD) and SIROQUANT were used to analyze the variation of mineral compositions of the floated coals. Quartz (SiO_2), kaolinite ($Al_2(Si_2O_5)(OH)_4$), calcite ($CaCO_3$), and tobelite ($NH_4Al_3Si_3O_{10}(OH)_2$) were main mineral which were found in Shanxi high ash coals, and the high contents of quartz and kaolinite led to high AFTs (ash fusion temperatures) of these coals. As mineral content decreased, the contents of quarts, kaolinite, and calcite in the floated coals were obviously lowered, and this resulted in the decrease of S/A (mass ratio of SiO_2/Al_2O_3) of the coal ashes. The ash fusion temperatures of Shanxi high ash coals were therefore significantly influenced by the extent of coal washing. Furthermore, the content of amorphous material in coals increased obviously with the decrease of ash content. These results have important implication in the selection of the appropriate coal washing procedure prior to gasification of these coals.

1. Introduction

The ash fusion temperature (AFT) of gasification feedstock is an important parameter for all gasifiers. For fluidised-bed gasifiers, the upper operating temperature is determined by AFT to avoid ash agglomeration [1]. For entrained-flow gasifiers, the operating temperature should be above the flow temperature (FT) of coal ash to ensure slag flow from the gasifier [2]. The AFT of a coal is largely dependent on its mineral compositions, which are strongly dependent on the chemical compositions of the coal ash. The effects of ash chemical compositions and mineral compositions on the AFT of coal have been widely studied both by means of the thermodynamic computer package FactSage and experimentally [3–5].

There are large reserves of Shanxi high ash coals in Shanxi province, China, which account for 40% of the coal reserve in Shanxi. The use of these high ash coals reserves is important for the security of energy supply, and therefore Shanxi high ash coals are expected to remain as a key energy source in the future. Gasification has been deemed as the most appropriate method for the utilization of these high ash coals, since it allows a more efficient and more environmentally friendly conversion of these coals [6,7]. It transforms chemical energy from the coal into value-added chemical products and liquid fuels as much as possible through syngas which mainly includes carbon monoxide and hydrogen [8]. However, owing to the high ash content, the use of these Shanxi high ash coals in gasification leads to a number of technical and economic challenges, e.g., high consumption of coal and oxygen, low syngas yield and cold gas efficiency [9–11].

To lower the ash content of the gasified coal, a common practice is to float the coal or wash with water or acid to remove some of the minerals originally present in the coal. Flotation is the most effective technology which is applied to reduce the sulfur content or ash content, and some excluded minerals can be removed by flotation [12]. There have been a considerable number of research articles published on flotation of coal and its allied research topics covering both basic

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http://dx.doi.org/10.1016/j.fuel.2017.10.046
Received 15 May 2017; Received in revised form 4 September 2017; Accepted 10 October 2017

science as well as on applied research [13–17]. Acid washing of coals is not used on a commercial scale, but it is an important method for the study of the effect of mineral matter on coal behavior. Hydrochloric acid (HCl) effectively removes most mineral matter, whilst hydrofluoric acid (HF) is effective in dissolving silicate minerals [18,19]. Washing with water is often used in upgrading of low rank coals, and it can remove some salts, like sodium chloride (NaCl) and magnesium sulfate ($MgSO_4$) [20,21]. When the ash content of these Shanxi high ash coals was reduced after treatment, the ash chemical compositions as well as the mineral compositions of these coals were influenced, which may results in the variation of the AFT of these Shanxi high ash coals. However, to the best of our knowledge, little research has been carried out to investigate the relation between ash content and ash fusion characteristics of Shanxi high ash coals.

In this work, three representative Shanxi high ash coals were floated with $ZnCl_2$ flotation agent to obtain floated coal samples with different ash contents. AFTs of the floated coal samples were determined and the chemical compositions of the floated coal ashes were analyzed by X-ray fluorescence (XRF). The floated coal samples were also ashed using a radio frequency oxygen plasma furnace to obtain low temperature ash (LTA). X-ray diffraction (XRD) and SIROQUANT were carried out to investigate the mineral compositions of the floated coal samples.

2. Experimental

2.1. Materials

Shanxi coals were rich in quartz and kaolinite, and some coals have a significant content of tobelite and calcite [22,23]. For this study, three representative Shanxi high ash coals were selected: Sihe9, Fenghuang9, and Sihe15 (denoted as SH9, FH9, and SH15, respectively). The ash contents of these coals were 41.67% (SH9), 31.72% (FH9), and 19.79% (SH15). These coal samples were ground to a particle size of less than 0.200 mm, dried at 105 °C for 24 h in a N_2 atmosphere. As specified in Chinese standards for coal analyses (GB/T212-2001, and GB/T476-2001, GB/T214-1996), the proximate analyses, ultimate analyses on the basis of air dry, and total sulfur content of the three coals were analyzed, and the results are given in Table 1.

Coal ashes of the three coals were prepared according to Chinese standard (GB/T1574-2001). Briefly, the coal samples were placed in a muffle furnace, heated to 500 °C within 30 min and kept at this temperature for 30 min, and then the temperature was increased to 815 °C and held at this temperature until the mass fluctuation is below 0.20 g. Thereafter, the coal ashes were taken out, and cooled. The chemical compositions of the three coal ashes were analyzed by XRF according to ASTM D 4326, and the results are presented in Table 2.

Table 1
Proximate and ultimate analyses of SH9, FH9, and SH15.

	SH9	FH9	SH15
Proximate analysis on an air dry basis (wt%)			
Fixed Carbon	49.19	58.95	71.64
Moisture	3.60	3.72	3.35
Ash	41.67	31.72	19.79
Volatile	5.54	5.61	5.22
Ultimate analysis on an air dry basis (wt%)			
Carbon	47.49	54.27	66.38
Hydrogen	1.81	1.96	2.30
Nitrogen	0.54	0.66	0.85
Sulfur[a]	1.69	3.89	2.83
Oxygen[b]	3.20	3.78	4.50

Note:
[a] : Total sulfur.
[b] : By difference.

Table 2
Ash compositions of SH9, FH9, and SH15.

Chemical compositions of ashes (wt%)	Samples		
	SH9	FH9	SH15
SiO_2	56.88	52.37	43.18
Al_2O_3	29.92	26.45	33.79
Fe_2O_3	5.35	13.21	10.41
CaO	2.70	2.69	7.31
MgO	0.66	0.63	0.33
TiO_2	0.95	0.92	1.08
SO_3	0.78	1.13	1.95
K_2O	1.49	1.37	0.82
Na_2O	0.86	0.71	0.13
P_2O_5	0.10	0.05	0.04

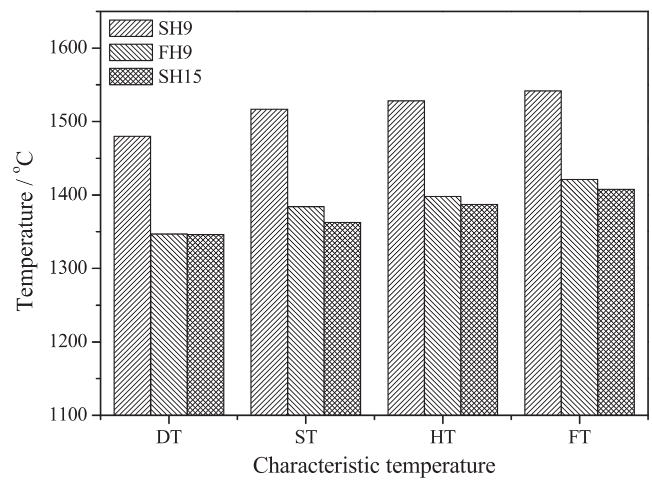

Fig. 1. AFTs of SH9, FH9, and SH15 under reducing atmosphere.

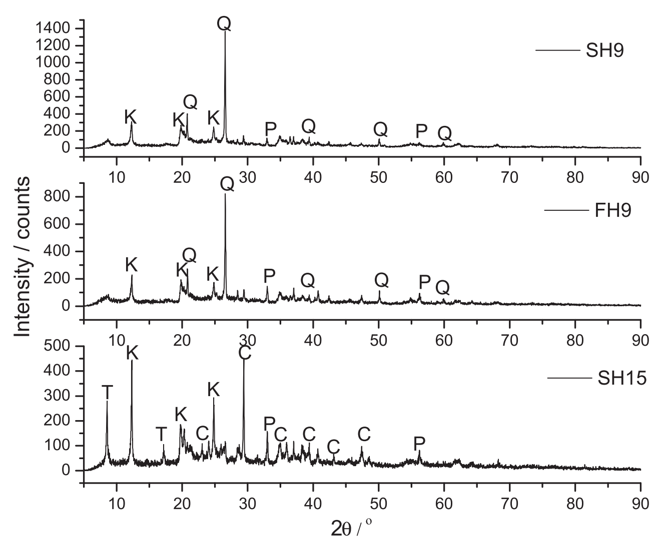

Fig. 2. XRD patterns of major minerals in LTAs of SH9, FH9, and SH15.

Table 3
Content of major minerals in the LTAs of SH9, FH9, and SH15 coals (wt%).

Samples	Amorphous	Quartz	Kaolinite	Pyrite	Calcite	Tobelite
SH9	46.30	25.10	24.00	4.60	–	–
FH9	43.10	21.90	21.00	14.00	–	–
SH15	50.32	–	21.80	10.95	11.33	5.59

–: undetected.