Fuel Processing Technology 92 (2011) 1042–1051

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Comparison of sintering and compressive strength tendencies of a model coal mineral mixture heat-treated in inert and oxidizing atmospheres

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ARTICLE INFO

Article history:
Received 14 July 2010
Received in revised form 2 November 2010
Accepted 30 December 2010
Available online 22 January 2011

Keywords:
Sintering
Minerals
$CaSO_4$
Compressive strength test
TG/DTA

ABSTRACT

The chemical interactions responsible for sintering in a coal mineral mixture were investigated in air and in N_2. A mineral mixture was made up by mixing kaolin, pyrite, quartz, calcite, hydromagnesite, $FeCO_3$ and anatase in a fixed ratio. The mineral mixture was pelletized and heat-treated up to 1100 °C in order to evaluate sintering by recording the compressive strength values and visual assessment with scanning electron microscopy (SEM). Chemical interactions responsible for the trends in the compressive strength results were investigated with simultaneous thermogravimetric and differential thermal analysis (TG/DTA), as well as X-ray diffraction. The results indicated that the formation of anhydrite ($CaSO_4$) was responsible for increased mechanical strength in the mineral mixture pellets heated in air at temperatures higher that 400 °C. $CaSO_4$ formed from the reaction of the decomposition products of pyrite and calcite (SO_x and CaO). The TG/DTA results also indicated that the reaction with pyrite in air caused the decomposition of calcite in the mixture at a lower temperature than was observed for calcite only. The pellets heated in N_2 did not increase in mechanical strength during heat-treatment due to the lack of $CaSO_4$ formation in the inert atmosphere. However, SEM analysis indicated that sintering did occur at the higher temperatures in N_2. A decrease was observed in the compressive strength values obtained in air at temperatures from 900 °C to 1100 °C. Reasons for the decreased compressive strengths may include increased porosity, decomposition of $CaSO_4$, and changes in the characteristics of the aluminosilicate phases.

1. Introduction

Coal consists of organic and inorganic matter in varying concentrations, and hosts a variety of different mineral species. The concentrations and types of minerals differ from one coal source to another. The most common mineral species found in coal include quartz, kaolinite, illite, montmorillonite, gypsum, siderite, calcite, dolomite and feldspars [1–10]. Depending on the technology, ash produced in combustion and gasification systems exits the reactors either as dry ash or a slag. Different combustion and gasification technologies are designed to handle different amounts of ash. Mineral matter in coal is not desired, but unavoidable. It is mined with the coal, but does not contribute to the value [8].

Differences in local temperature, atmosphere, heating rates and other minerals in close proximity cause included and excluded minerals to react differently during coal consumption [11,12]. Included minerals tend to coalesce with associated minerals in the char structure as the char is consumed [11,13,14]. Included minerals are the major source of glass phases in ash [15,16]. Excluded minerals generally experience fragmentation [14,17–19]. Fragmentation is a result of several mechanisms, including thermal shock, mechanical breakage, rapid gas release and inorganic reactions [14,19]. Several researchers have referred to limited interaction among excluded minerals based on the low probability of colliding [13,19]. However, Wang et al. [17,18] concluded that the proposed limited interaction is inconsistent when considering the fluxing promotion caused by calcium/iron-rich additives in high-temperature gasification. It was suggested that the excluded additive particles partly scavenge the inherent aluminosilicate species [17,18]. Kuramoto et al. [20] also found that included minerals reacted with added Ca-based CO_2 sorbents during the study of a novel steam gasification process.

Numerous mineral interactions participate in ash formation during coal utilization, and excluded minerals often consist of a mixture of minerals in a single grain [12]. Several studies have illustrated the importance of associated minerals during ash formation [13,21,22]. A study by Liu et al. [12] on Australian coals revealed that illite associated with kaolinite tends to swell and form cenospherical ash particles. The transformations of excluded mineral matter not only affect ash formation, but also have an influence on the particle size distribution (PSD) of the resultant ash [17,19,23]. The temperature-

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doi:10.1016/j.fuproc.2010.12.030

dependent interactions between minerals in coal can cause sintering and agglomeration when certain species occur at sufficiently high temperatures. The compressive strength test is the most common technique to evaluate or determine sintering in coal ash [24]. Sintering is usually accompanied by grain growth and an increase in the mechanical strength of sintered particles. Agglomeration and sintering in the reactor bed will result in an increase in the particle size of the bed material and ash. Sufficient particle growth and the formation of agglomerates may cause bed defluidisation in fluidized beds, ensuing interruptions to operation. Tendencies to form agglomerates are governed by the swelling index of the fuel, ash chemistry and operation temperatures [25]. However, agglomeration of ash particles may also aid operation in packed-bed reactors by providing favourable porosity to allow steam and oxygen through the ash bed [15].

The focus of the study was on the ash formation processes in the temperature range commonly found in fluidized-bed combustion. Fluidized-bed reactors require operation at temperatures well below the ash fusion temperature of the fuel, usually in the range of 800 °C to 1050 °C [25]. Ash particles inside the bed are in constant collision with each other, the reactant gases and the incoming fuel particles. Some of the interactions may be responsible for the formation of agglomerates. Agglomeration and sintering in the bed will result in an increase in the particle size of the bed material and ash. A mineral mixture was prepared consisting of common and abundant minerals in coal. An attempt was made to investigate the chemical interactions occurring during heating of the associated minerals, in order to explain the resultant tendencies in the compressive strength behaviour.

2. Material and methods

Experiments were performed in a temperature range conducive to sintering in the mineral mixture, as well as temperatures required for the operation of fluidized-bed reactors. Methods used to investigate sintering and agglomeration in the model mineral mixture included: compressive strength tests; simultaneous thermogravimetric and differential thermal analysis (TG/DTA); scanning electron microscopy (SEM); and X-ray diffraction (XRD).

2.1. Model mineral mixture

A model mineral mixture was prepared by mixing compounds representing the main minerals in coal in a fixed ratio. The mineral mixture consisted of 25% kaolin, 20% quartz (SiO_2), 20% pyrite (FeS_2), 15% calcite ($CaCO_3$), 8% $FeCO_3$, 8% hydromagnesite ($MgCO_3$, basic), and 4% anatase (TiO_2) by weight percentages. Table 1 lists the chemical compounds included in the mixture. A portion of the calcite together with the hydromagnesite represented dolomite. It is seldom that the concentration of TiO_2 is as high as 4% in coal mineral matter. However, the concentration was chosen to meet the detection limitations of analytical techniques. The compounds (as received) were mixed in the appropriate ratios and dried overnight at 100 °C. The mixture was sized to −355 μm. Weighing of the mineral mixture before and after drying yielded mass losses associated with moisture of between 1% and 2%.

2.2. Compressive strength tests

Compressive strength tests were performed on cylindrical pellets. At least six pellets were prepared in the same manner for heat-treatment at each temperature. Pellets were prepared in a 10 mm die set from 1 g of the mineral mixture. Drops of water were added to the mixture in the die set at intervals. The addition of water improved compression and prevented crumbling of pellet edges. The pellets were pressed by applying a force of 1500 N for 3 min on the die set, which was placed between compression plates. The force was applied with an Ametek Lloyd Instruments LRXplus strength tester equipped with a 5 kN loadcell.

The pellets for oxidizing compressive strength tests were heated in static air at 500 °C to 1100 °C (in 100 °C increments) and kept at the desired temperatures for 2.5 h. A Lenton muffle furnace equipped with a TOHO 300 micro-processor was used. The furnace was heated at 5 °C/min to the desired temperature. After completion of the temperature program, the pellets were left in the furnace to cool down to below 60 °C before removal.

Pellets were heat-treated under nitrogen in a ceramic tube furnace (Elite, UK model TSH15/75/610). Ceramic heat shields were inserted at both ends of the tube furnace to improve the stable temperature working area of the furnace. The ends of the tube furnace were enclosed by stainless steel caps with a gas inlet or outlet. The tube furnace with pellets was flushed with nitrogen for at least 15 min at a flow rate of approximately 1 L/min before each experiment. A nitrogen flow of approximately 500 mL/min was maintained for the duration of the experiments and the cooling period. The pellets were heated at 5 °C/min. Pellets were also heat-treated at 500 °C to 1100 °C (in 100 °C increments) and kept at the desired temperatures for 2.5 h. After completion of the temperature program, the pellets were left in the furnace to cool down to below 60 °C before removal.

The pellets, heat-treated (sintered) in air or nitrogen, were crushed at ambient conditions to record their compressive strengths. The Ametek Lloyd Instruments LRXplus strength tester used to prepare the pellets was also used to crush and record the compressive strength of each pellet. The speed of the compression plates was maintained at 10 mm/min during crushing to apply an increasing force on the pellets. The maximum force applied to incur breakage was recorded for each pellet. The average compression strength value was calculated for each sintering temperature. Several identical experiments were performed. The error bars associated with each average value represent 95% confidence limits. The compressive strength results are expressed as the maximum force divided by the area, or N/mm^2.

2.3. X-ray fluorescence spectroscopy

Major and minor elements of the compounds in the mixture were determined by X-ray fluorescence spectroscopy (XRF). The analyses were performed on a ThermoARL Model 9800XP, simultaneous/

Table 1
Chemical compounds representing minerals included in the model mineral mixture.

Name	Formula	Purity	Ratio (wt.%)	Supplier
Kaolin (heavy)	$Al_2Si_2O_5(OH)_4$	Ph. Eur. Bp	25	Riedel-de Haën
Quartz	SiO_2	Purum p.a. sand	20	Fluka
Iron disulfide	FeS_2	95 %	20	Strem Chemicals
Calcium carbonate	$CaCO_3.nH_2O$	98.0–100.5 %	15	Merck
Ferrous carbonate	$FeCO_3.nH_2O$	Laboratory reagent	8	Qualikems
Magnesium carbonate, basic	$MgCO_3.nH_2O$	Meets USP testing specifications	8	Sigma
Titanium (iv) oxide	TiO_2	–	4	Sigma