Journal of Analytical and Applied Pyrolysis 121 (2016) 376–386

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Investigation on the effect of particle size and heating rate on pyrolysis characteristics of a bituminous coal by TG–FTIR

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ARTICLE INFO

Article history:
Received 22 December 2015
Received in revised form 15 August 2016
Accepted 22 August 2016
Available online 23 August 2016

Keywords:
Coal
TG–FTIR
Particle size
Heating rate
Devolatilizaion
Evolved gas analysis

ABSTRACT

In this work, thermal behavior of five different coal particle fractions were investigated using thermogravimetric analyzer (TGA) under various heating rates with the maximum of 1000 K/min. An on–line Fourier Transform Infrared Spectrometry (FTIR) was employed to evaluate the evolution characteristics of the gaseous products. The results showed that the coal particle size remarkably affected the mass loss and the ash amount. The larger the particle size was, the higher mass loss and the more ash could be, which revealed its high pyrolysis reactivity. In addition, with increasing the particle size, the initial devolatilization temperature (T_{in}) and devolatilization index (D_i) increased, whereas, the final devolatilization temperature (T_f) decreased. This phenomenon was explained by a proposed mechanism of the obstacle escaping of volatiles from the interparticles corresponding to forming large block unit of metaplast. The heating rate has significant effect on the performance of devolatilization profiles and gaseous products releasing. T_{in}, T_{max} and T_f displayed the logistic distribution along with heating rate up to 1000 K/min, whereas, R_{max} and the heating rate were highly linear correlated with different particle fractions. The enhanced yield at maximum releasing rate for all the gas species were observed with increasing the heating rate. Moreover, the peak of maximum releasing rate on the evolving profiles of gaseous products became narrower and sharper, and releasing time of the gaseous products reduced extremely with increasing the heating rate. These findings can provide fundamental data for practical applications, plant designing, handling, and modeling of integrated coal fluidized bed gasification system as well as other coal fluidized bed pyrolysis/gasification process.

1. Introduction

The huge consumption of coal over the past few decades has caused serious environmental impact locally and globally such as acid gases emission, global climate change and haze weather. The coal consumption proportion continued to hold the first place (64.2%) in primary energy, even though the total coal consumption fell by 2.9% during 2014 in China [1]. Thereby, coal will continue to play a key role in China's energy source for a relatively long time, not only for power generation, but also for production of fuels and chemicals. In order to balance this confrontation state between environment problems and amounts of coal consumption, it is very critical for clean and efficient utilization of coal.

The pyrolysis of coal has attracted much attention because it is the process to produce valuable products such as liquid fuels, fuel gases and some other chemicals. Furthermore, the pyrolysis process is the initial step in coal carbonization, liquefaction, combustion and gasification. The softening, swelling, agglomeration characteristics of coal particles are also related to the coal pyrolysis [2]. In addition, the pyrolysis reactions can provide basic information concerning thermal decomposition of individual functional groups and the coal molecular networks [3]. Cascade conversion of coal combining pyrolysis and gasification in an integrated fluidized bed reactor can produce methane–rich syngas using powder coal particles [4]. The released volatiles control the ignition, temperature, and stability of the flame which can consequently influence the fluidization conditions when it comes to the different particle sizes of coal. In such systems, comparing to other parameters such as pressure, atmosphere and residence time etc., the influ-

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http://dx.doi.org/10.1016/j.jaap.2016.08.020
0165-2370/

ences of coal particle size and heating rate are more significant factors because of the variations of the heat and mass transfer inside or among the coal particles during devolatilization [5], which will affect the gaseous products distribution in pyrolysis and the characteristic of char gasification. Moreover, variations of mineral matter component and content, maceral composition and volatiles often exit in the different coal particle fractions simultaneously, which consequently affect the pyrolysis characteristics [6]. As for caking bituminous coals, the swelling behavior is strongly related to the coal particle sizes, and the swelling ratio increases with the decrease of the size of coal particles due to the enrichment of vitrinite in smaller particles [7]. Many researchers have evaluated the particle size distribution on releasing characteristics of gaseous products during coal devolatilization. Morris and Pather [8] reported that the particle size instead of bed depth is dominant in determining the yields of methane and carbon dioxide. The same result was also obtained when using a quartz fixed bed reactor at higher temperature (between 1000 and 1150 °C) [9]. In another investigation, Liu et al. [10] suggested that the amounts of CO decrease with increasing of coal maturities and particle sizes, which is consistent with the pore volume distributions in coal. Furthermore, large numbers of deep investigations were conducted on the mass and heat transfer during pyrolysis of different coal particles. Generally, with the decrease of coal particle sizes, the diffusion distance and resistance decrease, and the heat/mass transfer rate increases remarkably [11]. Due to impedence of internal heat conduction, the internal temperature distribution of large coal particle differs obviously, so the starting pyrolysis time of the center is much later than the external layer of coal, consequently, the different yields of volatiles will generate in different coal particle radius directions [12,13]. Moreover, the performance of char and its gasification characteristics are also influenced by the size of the coal particles, especially in the spouted bed reactor [14,15].

Heating rate is another important factor of coal devolatilization process. The maximum mass loss rate and the releasing rate of gaseous species are generally affected by means of the alterations of heating rate profoundly during primary pyrolysis stage (300–600 °C) [16]. Lower sulfur in char could be achieved by pyrolysis at higher heating rate of coal due to acceleration of the releasing rate of organic sulfur [17]. Heating rate can significantly affect liquids yield during coal pyrolysis. Gibbins and Kandiyoti found that tar yield from pyrolysis of a bituminous coal increased when the heating rate increased sufficiently in a wire–mesh pyrolysis apparatus [18]. Yan et al. [19] have reported that the increase in heating rate resulted in the greatly increase in yield of light gases as well as coal conversion in the drop tube furnace and plasma reactor. However, Suuberg et al. [20] observed that heating rate has insignificant influence on the yield of the pyrolysis products. The similar result was also obtained that the pyrolysis yield of the Ca–form and Na–form coal samples did not show significant heating rate sensitivities [21]. The contradictory results with regard to heating rate might be often arised due to the secondary reactions from volatiles char interactions which cannot be prevented in experimental systems as well as the coal type. The nature of coal structure makes it very difficult to conduct clear experiments to determine the conversion rates, mechanisms and volatiles in coal pyrolysis. Although previous investigations associated to particle size and heating rate on the pyrolysis properties of coal have achieved great process and a number of experimental and theoretical approaches have been used to further elucidate pyrolysis mechanism of coal under various conditions [22]. The fundamental knowledge of influences of particle size and heating rate on mass losses, characteristic parameters and gaseous products releasing during pyrolysis process has not been fully understood, especially for upper limit of heating rate at high region (up to 1000 K/min).

TGA is widely used in physical chemistry, materials research, and thermal analysis. It provides findings on volatilization behavior over a wide range of temperatures, and mostly it has been used to describe the profiles, such as the initial decomposition and terminated temperatures for various decomposition reactions [23]. Moreover, TGA has been successfully used in quantitative analysis of the gas products by combining gas–phase FTIR spectroscopy during the thermal degradation process of fossil fuels due to its fast and very sensitive for detection of organic volatile matter, apart from paramagnetic diatomic molecules. It provides important information on the devolatilization of materials, i.e. the identification of major volatile species and the typical temperature range of release with a continuous measurement and the mass changes can be correlated with the identification of what kind of volatile or gas is released during a specific thermal event [24]. Thereby, during thermochemical conversion of different coal particles, the composition of the gaseous products can be carried out using the on–line combination of TG and FTIR.

In this work, five different particle size fractions originated from a bituminous coal are pyrolyzed on a fast speed thermogravimetric analyzer coupled with an on–line FTIR with the heating rates from 8 K/min up to 1000 K/min. The characteristic parameters derived from thermal behavior profiles and gaseous species evolution profiles as a function of coal particle sizes and heating rates were comprehensively investigated and the experimental phenomena were also interpreted with reasonable mechanism. The objective of this study is to gather data and obtain knowledge, which can be useful in modeling, designing and running of cascade conversion utilization technology for producing methane–rich syngas by combining pyrolysis and gasification of coal in an integrated fluidized bed reactor.

2. Experimental section

2.1. Coal samples

A bituminous coal, Shandong raw coal (SD) was used in this study in the Shandong province of China. The coal was firstly crushed to millimeter size in a jaw crusher, and then portions of the millimeter sized coal samples were sun–dried before being grounded to micrometer size in a planetary ball mill. Both the crushed and grounded coal powder were put in the top of a set of laboratory sieves stacked vertically in descending order of decreasing mesh size with a collector pan at the bottom, and it was sieved for 30 min using an orbital shaker. The sizes of the sieves were 1400, 840, 250, 150 and 74 μm, respectively. Then five different fractions of the coal sample were obtained, that is, 1400–840, 840–250, 250–150, 150–74 and <74 μm. Proximate analysis of each particle size fractions were carried out using TGA procedure reported previously [25]. Ultimate analysis of each samples were performed in a Vario macro cube elementar apparatus. The properties of each particle size fractions are listed in Table 1.

2.2. Pyrolysis method

The pyrolysis experiments of different particle diameter coal samples were carried out on a thermogravimetric analyzer (STA449F3, NETZSCH–Gerätebau GmbH, Germany) coupled with a Fourier Transform Infrared Spectrometer (Bruker Tensor 27, Bruker, Germany). Prior to the thermal investigation, the instrument is calibrated using indium/aluminum check method. In a typical run, about 10 mg samples were used and temperature was raised from room temperature to 110 °C at a heating rate of 15 K/min, and then maintained at this temperature for 20 min to remove the moisture content. Subsequently, the samples were