Journal of the Energy Institute xxx (2016) 1–12

Contents lists available at ScienceDirect

Journal of the Energy Institute

journal homepage: http://www.journals.elsevier.com/journal-of-the-energy-institute

Air and oxy-fuel combustion kinetics of low rank lignites

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ARTICLE INFO

Article history:
Received 8 September 2016
Received in revised form
9 November 2016
Accepted 14 November 2016
Available online xxx

Keywords:
Lignite
Oxy-fuel
Combustion
Thermogravimetry
Kinetics

ABSTRACT

The air and oxy-fuel combustion processes of two low-grade lignite coals were investigated by thermogravimetric analysis (TGA) method. Coals were provided from two different coal mines in the Aegean region of Turkey. Oxy-fuel combustion experiments were carried out with three different gas mixtures of 21% O_2–79% CO_2; 40% O_2–60% CO_2 and 50% O_2–50% CO_2 at 950 °C and heating rates of 10 °C/min, 20 °C/min and 40 °C/min. The kinetics of the oxy-fuel combustion of coals were studied by using four different methods namely, Coats-Redfern (model-fitting method), Friedman (FR), Flynn–Wall–Ozawa's (FWO) and Kissinger–Akahira–Sunose's (KAS) methods. The apparent activation energies of combustion process calculated by FWO method are slightly but systematically higher than that calculated by the KAS and FR methods for the oxy-fuel atmospheres. Combustion behavior of both coals in the oxy-fuel combustion environment could vary significantly, likely due to their characteristics such ash and volatile matter contents.

1. Introduction

Global coal consumption fell by 1.8% in 2015, well below the 10-year average annual growth of 2.1% but it is still the fastest-growing fossil fuel consumption. Coal's share of global primary energy consumption fell to 29.2%, the lowest share since 2005. Nowadays, demand for electric power continues to increase due to population growth, technological and economical development. So do the environmental pollution and concerns. With 891 billion tons of proved coal reserves, coal combustion has an important role in energy production worldwide [1]. However, coal combustion produces a large amount of CO_2, which is the chief contributor to global climate change. In order to achieve future targets for the reduction of greenhouse gas (GHG) emissions, CO_2 must be captured and stored. Several strategies for the reduction the amount and capture of CO_2 from large-scale stationary power plants are currently being studied. The oxy-fuel combustion of coal with recycled flue gas is considered as a promising option to ensure the continued use of coal for energy (heat and electrical power) production. Conventional coal-fired boilers use air for combustion which produces a flue gas stream with a diluted CO_2 concentration of typically 14–16%, due to presence of nitrogen in the air. Therefore, these flue gases are not suitable for direct CO_2 sequestration and storage. In the oxy-fuel combustion, fuel is burnt in a mixture of oxygen and the recycled flue gas yielding a CO_2 (95%)-rich stream, which after purification and compression becomes suitable for sequestration. An important advantage of this technology is that it avoids the formation of thermal NOx due to the absence of nitrogen in the combustion atmosphere and substantially reduces the NOx emissions. In addition, the oxy-fuel combustion requires only minor modifications of the existing pulverized coal combustion technology that has already demonstrated its reliability and won widespread industrial acceptance [2].

The coal combustion in O_2/N_2 and O_2/CO_2 atmospheres has received quite extensive attention and has been studied [3–13]. Studies indicated that coal combustion reaction rate was considerably reduced when N_2 was replaced by CO_2 at the same oxygen concentration level. The devolatilization time of coal, was reported not to be affected by the substitution of N_2 with CO_2 under suspension-fired conditions. The burnout times of pulverized char at identical O_2 concentration, however, were found to be longer in an O_2/CO_2 atmosphere compared to O_2/N_2 mixtures [10]. These differences were thought to be originating from the higher heat capacity of CO_2, the lower diffusivity of gaseous components in an enriched CO_2 atmosphere [11,12] and the endothermic char gasification reaction with CO_2 [10]. The difference between

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http://dx.doi.org/10.1016/j.joei.2016.11.004
1743-9671/

Please cite this article in press as: B. Engin, H. Atakül, Air and oxy-fuel combustion kinetics of low rank lignites, Journal of the Energy Institute (2016), http://dx.doi.org/10.1016/j.joei.2016.11.004

the devolatilization times in the oxy- and air atmospheres, however, was found to be almost negligible for the pulverized fuels with high volatile contents [13].

The thermogravimetric analysis (TGA) is a common technique used to investigate and compare thermal behavior and to determine kinetic parameters of the combustion, pyrolysis and gasification of solid raw materials, such as coal, wood, biomass etc. Moreover, quantitative methods can be applied to TGA results to obtain kinetic parameters of the thermal events [14].

Lignite coals, with a reserve of about 12 billion metric tons, are the major and the most important fossil fuel resources of Turkey. However, they are poor quality coal with low calorific value, high moisture, volatile matter, ash and sulfur contents. On the original basis, almost 75% of these reserves have calorific value lower 2000 kcal/kg, 17% of them have 2500–3000 kcal/kg calorific value and only 8% have a calorific value higher than 3000 kcal/kg [15]. Therefore, they are causing huge environmental problems when they used as fuel for energy generation by conventional combustion methods. Fluidized bed technology combined with oxy-fuels combustion appears very promising for a clean use of these coals. No study has been done on the oxy-fuel combustion of them in fluidized bed combustor. We currently conduct an experimental study on the oxy-fuel fluidized bed combustion of lignites. This work is a part of this study. The aim of the present work is to study the oxy-fuel combustion characteristics of the lignites. For this purpose, thermogravimetric analyses of the coals were conducted under varying operating conditions. Experimental results were analyzed by using different methods, namely Coats-Redfern, (model-fitting method), the isoconversional meethods (model-free methods), Friedman, Flynn–Wall–Ozawa's (FWO) and Kissinger–Akahira–Sunose's (KAS) methods, to determine the kinetic parameters which represent the oxy-fuel combustion characteristics of the coals under an oxygen-carbon dioxide atmosphere.

2. Materials and methods

2.1. Lignite coal samples

Two representative Turkish coals were selected from two different coal mines, supplied from Aegean Lignite Enterprise and Seyitomer Lignite Enterprise both in Aegean part of Turkey and were used in the combustion experiments. These lignites were named AL and SL, respectively. The original fuels were air-stabilized, ground and repetitively sieved under 70 μm size. The samples were prepared according to ASTM D 2013/D 2013 and stored in sealed containers for TGA experiments. The proximate, ultimate and calorific value analyses of coals were conducted according ASTM D 7582 and ASTM D 5373 and ASTM D 5865 standard methods, respectively. Results of these analyses were presented in Table 1. As seen from the table, both fuels are typical low grade coals characterized by their high ash, high volatile matter, low carbon contents and low calorific values. The SL, however, is relatively superior than the AL coal in respect of all parameters except sulfur content.

2.2. Experimental setup and method

Thermogravimetric experiments were carried out in a Mettler Toledo International Inc, TGA/SDTA851e type apparatus under varying operating conditions. In the experiments, previously prepared samples were heated in a furnace enclosed by a cooling jacket. Several experiments without samples were carried out and used as a background in order to subtract the buoyancy effect.

In each run, about 10 mg of fuel sample was heated with a heating rate of 10, 20 and 40 °C/min from the room temperature up to 950 °C and were held at this temperature for 30 min to ensure that the weight loss ended and weight curves leveled. The targeted combustion gas mixtures were prepared by mixing of two gases, oxygen and carbon dioxide which were supplied from gas cylinders. Gases, whose flow rates were measured and regulated by mass flow controller, then fed to the combustion chamber of the apparatus. The total gas flow was set to 40 ml/min in all experiments.

Thermogravimetric combustion experiments were carried out in both the air and the oxy-fuel environments. The results of coal combustion runs conducted in the air environment were used as benchmarking cases for comparison purpose. These runs were identical to that of the oxy-fuel combustion in which N_2 was replaced by CO_2. The oxy-fuel combustion experiments were carried out under three different combustion atmospheres: 21% O_2–79% CO_2, 40% O_2–60% CO_2 and 50% O_2–50% CO_2. In addition, combustion runs with pure oxygen (100%) were also conducted in order to investigate combustion behavior of coals under extreme conditions without presence of N_2 and CO_2 and use the results for benchmarking.

3. Theory

There are different methods being used to analyze kinetic data obtained from combustion experiments. Two approaches are frequently used for this purpose: model-fitting and isoconversional (model-free). Results obtained from experimental studies were evaluated by using

Table 1
The proximate and the ultimate analyses of AL and SL.

Coal	Proximate analysis (db[a], wt%)			Heating values (db[a], kcal/kg)	
	Volatile matter	Ash	Fixed carbon	Higher heating value	Lower heating value
SL	40.41	28.27	31.32	4802	4600
AL	33.26	40.46	26.28	3781	3621
Coal	Ultimate analysis (db[a], wt%)				
	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen[b]
SL	53.70	2.74	1.12	2.51	11.66
AL	43.72	3.05	0.84	0.92	11.19

[a] db: dry basis.
[b] The oxygen content was calculated by difference.