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Effect of Atmosphere on Volatile Emission Characteristic in Oxy-Fuel Combustion

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ABSTRACT

A new type of power supply which was called oxy-fuel combustion power plant was introduced to reduce greenhouse gasses emission. In this paper the volatile emission characteristic of pulverized coal is studied under air atmosphere and oxy-fuel atmosphere. Combustion experiments of Datong bituminous coal were carried out in a wire mesh reactor at heating rates of 1 K/s, 10 K/s and 1000 K/s respectively under air and O_2/CO_2 atmosphere conditions in order to investigate the volatile emission characteristic. The concentrations of volatile (mainly CO and CH_4) emission were on-line measured by infrared gas analyzer. It was indicated that the concentrations of CO and CH_4 in O_2/CO_2 atmosphere were higher than those in air. The direct oxidation of carbon and gasification reaction between carbon and CO_2 are the main causes of the increased amount of CO. The higher concentration of CO_2 also results in the increased amount of CH_4 in O_2/CO_2 conditions.

Keywords: Oxy-Fuel Combustion; O_2/CO_2 Atmosphere; Volatile Emission; Gasification Reaction

1. Introduction

The effect of greenhouse gasses on global climate change has resulted in the development of new technologies with lower emissions that can accommodate capture and sequestration of carbon dioxide [1,2], development of clean energy, smart grid and low-carbon economy has become a common choice for the world. Smart grid will penetrate new types of technologies into power supply side, power grid side and power consumer side to promote the carbon reduction in power systems through coordination of multiple technologies [3-5]. In this paper the specific technical path for a smart grid to achieve low-carbon power system are proposed based on clean production, a new type of power supply called oxy-fuel combustion power plant was introduced. Oxy-fuel combustion and CO_2 capture from flue gases is a near-zero emission technology that can be adapted to both new and existing pulverized coal-fired power stations. It can produce a sequestration ready high-CO_2-concentration effluent gas, and CO_2 can be utilized in depleted oil and gas reservoirs to increase their production or storage in deep ocean and saline aquifers. Oxy-fuel combustion is less expensive for retrofitting existed plant than the other considered options [6-10].

CO production is an important reaction in the coal combustion process, CO/CO_2 product ratio is a major factor that influence the combustion temperature and released energy, CO/CO_2 product ratio is also one of the basic research difficulties of coal combustion [11,12]. Carbon can be oxidized either to carbon monoxide or to carbon dioxide, the proportion to which carbon converts to either of the two products on the particle surface is still open to debate. CH_4 emission characteristics have an important influence on pulverized coal ignition mechanism as the major component of volatile. Therefore, the generation of CO and CH_4 has a major impact on combustion heat release and combustion reactions during pulverized coal combustion process [13].

Experimental and simulation studies have been carried out on CO production in the pulverized coal combustion process under air condition [14,15]. However, the reaction of carbon with oxygen is a continuous process, including heat, low temperature oxidation, ignition and combustion process. The measurement of CO is very difficult since carbon monoxide can be further oxidized in the reactor far from the burning particle. In addition, due to the limitations of the test conditions, previous studies were difficult to achieve precise control of particle heating rate, previous studies were also difficult to study CO/CH_4 formation characteristics under different heating rates.

The volatile emission characteristic of pulverized coal is very important for understanding how to switch existing burners from air to oxy-fuel combustion, The volatiles typically carry about 50% of the energy of the fuel, and in addition to heat release, the volatile oxidation is important for ignition. It is well studied under O_2/N_2 atmosphere, but under oxy-fuel atmosphere it haven't been recognized clearly [16,17]. In oxy-fuel combustion pulverized coal burns in O_2/CO_2 environment with higher CO_2 concentration, instead of O_2/N_2 environment. Because of the high toxicity of CO, it is very important to research whether O_2/CO_2 combustion lead to more CO emissions. Recently, CO emission characteristics under O_2/CO_2 combustion and conventional air combustion were studied by many scholars. Zheng *et al*. [18] did simulation study of CO production in O_2/CO_2 by FACT, but there is a lack of experimental verification. Wang [19] did combustion experiments using a 3 MW level furnace in the same flame temperature under air and O_2/CO_2 atmosphere, the results showed that there is no great difference of CO content in the flame and flue gas, but modeling results suggested that the flame CO content increased 5 times in flame under O_2/CO_2 atmosphere. Woycenko *et al*. [20] did the experiments at a 2.5 MW combustion furnace of IFRF found that CO content increased a lot in the flame zone, but the CO already burn out completely at the furnace exit, there is no observed significant CO emission. Because of the ignition delay and low peak temperature, when the oxygen content is reduced from 30% to 21%, CO emissions increased from 34 ppmv to 200 ppmv. Glarborg *et al*. [21] did natural gas combustion experiments, the results showed that even if the excess oxygen exist, the high CO_2 concentration in the O_2/CO_2 combustion at high temperatures can also prevent fuel (CO) was completely oxidized to CO_2, its inhibitory effect is most obvious in the fuel-rich area.

The general experiments measured the total amount of the CO in the whole reaction process rather than the instantaneous value, therefore they can not reflect the actual CO formation regularities. Because of the presence of secondary reactions in pulverized coal combustion process, CO can be oxidized to CO_2 on the surface of coal particles. It is very difficult to research the basis process of coal combustion in O_2/CO_2 atmosphere.

In this paper, the unique advantages of the wire mesh reactor were used. As was described in more details below [22], the wire-mesh reactor features a relatively accurate control of particle time-temperature history in the absence of significant secondary reactions of volatiles. The measurement of CO and CH_4 formation characteristics during pulverized coal combustion can be very accurate in air and O_2/CO_2 combustion.

2. Materials and Methods

In our study Datong bituminous coal was used, the proximate and ultimate analyses were given in **Table 1**.

The details of the experimental process can be found in our recent work [22,23], the combustion experiments were carried out in a wire mesh reactor, 30 mg coal sample was distributed between two layers of wire mesh. The wire mesh reactor was heated at a rate of 1 K/s, 10 K/s, 1000 K/s to 1273 K/s separately, while a stream of air (or 21% O_2/79% CO_2) mixture continually passed through the mesh at 4.0 L/min (measured under ambient conditions) to carry the evolved gas away. The concentrations of volatile (mainly CO and CH_4) emission were on-line measured by infrared gas analyzer.

Table 1. Properties of coal used.

	Datong
Proximate analysis[a] % (wt, dry)	
VM	26.7
FC	63.9
A	9.4
Ultimate analysis % (wt, dry)	
C	71.94
H	4.37
N	0.79
S	0.35
O[b]	13.15

[a]VM, volatile matter; FC, fixed carbon; A, ash; [b]By difference.

3. Results and Discussion

3.1. Effects of Reaction Atmosphere on CO Emission Characteristics

In this paper we studied CO emission characteristics of Datong bituminous coal in air and O_2/CO_2 atmosphere with a wire mesh reactor heated at a rate of 1 K/s, 10 K/s, 1000 K/s to 1273 K/s separately, results are shown in **Figures 1**-**3**.

It can be seen that CO emission concentrations of Datong bituminous coal were higher in O_2/CO_2 atmosphere than in air atmosphere both under slow heating and fast heating rates. When the reactor was heated at a rate of 1 K/s, the highest concentration of CO in air atmosphere appeared at 863 K, the highest value of CO concentration is 3270 ppm, in O_2/CO_2 atmosphere the highest value of CO concentration is 4045 ppm as shown in **Figure 1**. In O_2/CO_2 atmosphere CO concentrations are generally higher than in traditional air atmosphere, the maximum value is about 23.7% higher. When heated at a rate of 10 K/s, the highest concentration of CO in air atmosphere appeared at 923 K, the highest value of CO concentration is 2464 ppm, in O_2/CO_2 atmosphere the highest concentration of CO in air atmosphere appeared at 1073 K, the highest value of CO concentration is 7842 ppm which is 3.18 times than that in air atmosphere as shown in **Figure 2**. When heated at a rate of 1000 K/s, the highest value of CO concentration in air atmosphere is 957.4 ppm, in O_2/CO_2 atmosphere the highest value of CO concentration is 6023.1 ppm which is 6.3 times than that in

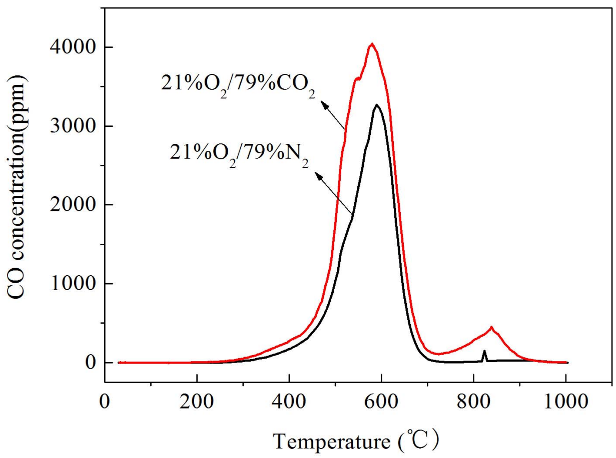

Figure 1. CO emission characteristics with a heating rate of 1 K/s.

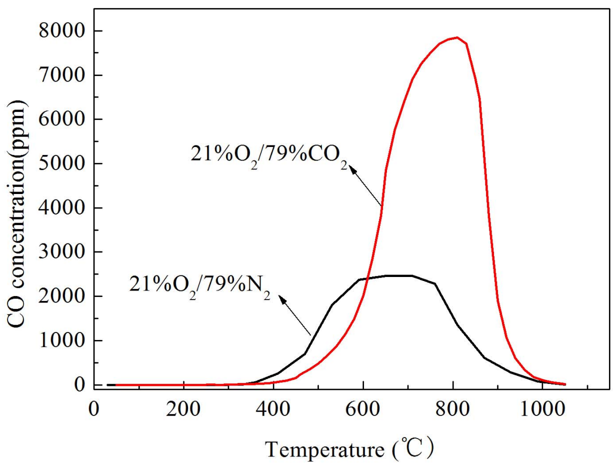

Figure 2. CO emission characteristics with a heating rate of 10 K/s.

air atmosphere as shown in **Figure 3**.

We found that when the coal was heated at a rate of 10 K/s, the ignition temperature of Datong bituminous coal is 855.99 K (T_1) in air atmosphere, the ignition temperature of Datong bituminous coal is 891.73 K (T_2) in O_2/CO_2 atmosphere. That means the temperature corresponds to the maximum CO concentration value is higher than the ignition temperature of pulverized coal, CO concentration continue to rise after coal ignition. In the low-temperature range, CO was produced from volatile emissions and direct oxidation of carbon, CO can be oxidized to CO_2 in the presence of oxygen.

CO generate reactions are as follows:

1) Carbon direct oxidation to CO:

$$C + 0.5O_2 \rightleftarrows CO \quad (1)$$

2) Because of the existence of the high concentration CO_2 gas in O_2/CO_2 atmosphere and the existence of partly high temperature area, carbon and CO_2 gasification generates CO

$$C + CO_2 \rightleftarrows 2CO \quad (2)$$

3) The gasification reaction of carbon and water

$$C + H_2O \rightleftarrows CO + H_2 \quad (3)$$

4) The reaction of CO_2 and H radical

$$H + CO_2 \rightleftarrows CO + OH \quad (4)$$

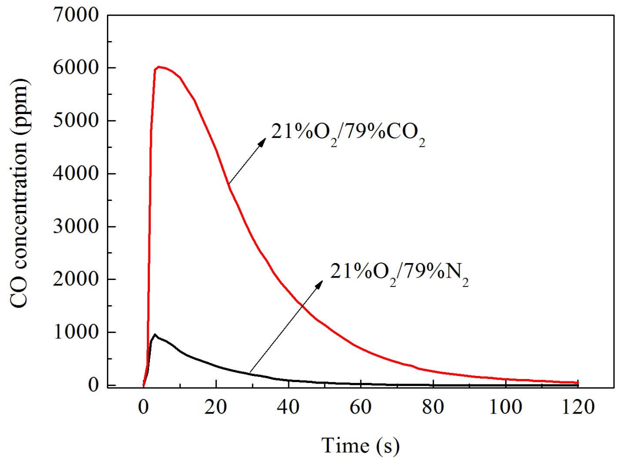

Figure 3. CO emission characteristics with a heating rate of 1000 K/s.

CO_2 is not inert but participates in chemical reactions, reactions of CO_2 with free radicals may proceed at lower temperatures. The most important step is the reaction with atomic hydrogen (Equation (4)) which is comparatively fast even at medium temperatures. The reactions of CO_2 with hydrocarbon radicals, will contribute to CO formation in the near-burner region under oxy-fuel combustion conditions. The higher levels of CO in this region may conceivably increase local problems with corrosion and slag, depending on the burner geometry and strategies for oxygen and flue gas. It would also be expected that the full oxidation of CO to CO_2 would occur further downstream in the furnace compared to conventional combustion [24-26]. Reactions between CO_2 and CH_2 radicals may also attribute to the increase of CO content in the flame zone, but because of the less number of free radicals that reaction would not be expected to be the dominating reaction for the increasing of CO content.

In O_2/CO_2 combustion of coal the above reaction all exist, the thermal decomposition of CO_2 is not the main reason for CO content increases in the flame. In O_2/CO_2 combustion due to the presence of high concentrations of CO_2 and partial area with high temperature, gasification reaction between carbon and carbon dioxide generate CO is more likely to occur than air combustion. Therefore, the direct oxidation of carbon and gasification reaction between carbon and CO_2 is the main reason for the increasing of CO content in oxy-fuel combustion.

3.2. Effects of Reaction Atmosphere on CH_4 Emission Characteristics

CH_4 is an important component of the volatile during pulverized coal combustion and pyrolysis process, the CH_4 emission characteristics is very important for understanding the combustion process of pulverized coal in air and O_2/CO_2 combustion. We studied CH_4 emission characteristics of Datong bituminous coal in air and O_2/CO_2 atmosphere with a wire mesh reactor heated at a rate of 1 K/s, 10 K/s,1000 K/s to 1273 K/s separately, results are shown in **Figures 4-6**.

It can be found that CH_4 emission concentrations of Datong bituminous coal were higher in O_2/CO_2 atmosphere than in air atmosphere both under slow heating and fast heating rates. When the reactor was heated at rate of 1 K/s, the highest value of CH_4 concentration is 75.6 ppm in air atmosphere, in O_2/CO_2 atmosphere the highest value of CH_4 concentration is 107.19 ppm as shown in **Figure 4**. In O_2/CO_2 atmosphere CH_4 concentrations are generally higher than in traditional air atmosphere, the maximum value is about 41.8% higher. When the reactor was heated at rate of 10 K/s, the highest value of CH_4 concentration is 1104 ppm in air atmosphere, in O_2/CO_2 atmosphere the highest value of CH_4 concentration is 1694 ppm which is about 41.8% higher than that under air condition as shown in **Figure 5**. When heated at a rate of 1000 K/s, the highest value of CH_4 concentration in air atmosphere is 318.7 ppm, in O_2/CO_2 atmosphere the highest value of CH_4 concentration is 960.2 ppm which is 3.01 times than that in air atmosphere as shown in **Figure 6**. So we can say that in O_2/CO_2 the CH_4 emission concentrations were higher than that in air atmosphere.

Coal pyrolysis process is consist of some weak bonds breaking in macromolecules of coal at high temperature, then light gaseous substances, tar, etc release. The weakest depolymerization to generate small molecule chain occurred in early pyrolysis process, the occurrence of medium temperature cross-linking generating CH_4. Another process in early pyrolysis is the functional group decomposition generating CH_4, CO, H_2 and other gases. Reaction atmosphere affect coal pyrolysis process, atmosphere has an impact on pyrolysis products through secondary reactions. In O_2/CO_2 combustion, the presence of high concentrations of CO_2 promotes the formation of CH_4, therefore leading to the increase of CH_4 concentration in oxy-fuel combustion.

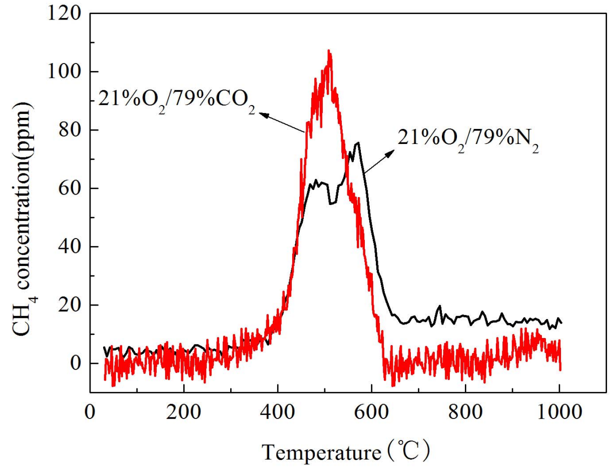

Figure 4. CH_4 emission characteristics with a heating rate of 1 K/s.

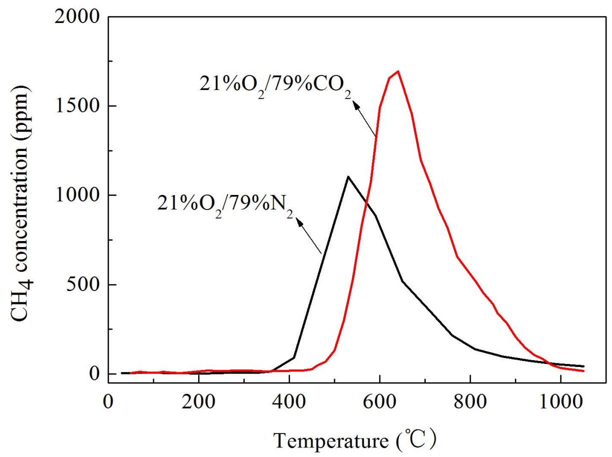

Figure 5. CH_4 emission characteristics with a heating rate of 10 K/s.

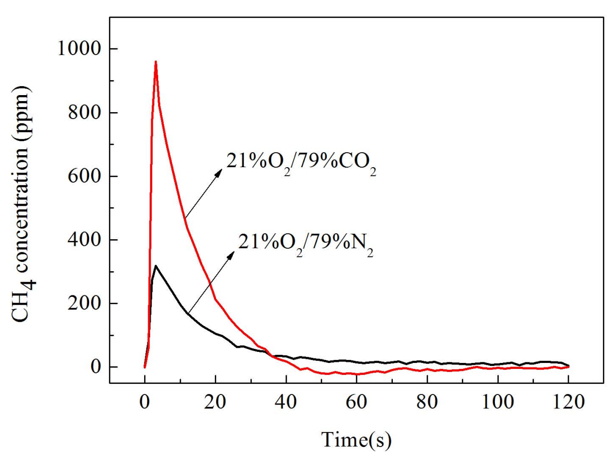

Figure 6. CH_4 emission characteristics with a heating rate of 1000 K/s.

4. Conclusions

Combustion experiments of Datong bituminous coal were carried out in a wire-mesh reactor at heating rates of 1 K/s, 10 K/s and 1000 K/s respectively under air and O_2/CO_2 atmosphere conditions. The concentrations of CO and CH_4 emission from the coal were on-line measured by infrared gas anlyzer. The following main conclusions can be drawn: 1) the concentrations of CO and CH_4 in

O_2/CO_2 atmosphere were higher than those in air. The direct oxidation of carbon and gasification reaction between carbon and CO_2 are the main causes of the increased amount of CO; 2) the higher concentration of CO_2 also results in the increased amount of CH_4 in O_2/CO_2 conditions.

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