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Research article

A kinetic study on the catalysis of KCl, K_2SO_4, and K_2CO_3 during oxy-biomass combustion

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ABSTRACT

Biomass combustion under the oxy-fuel conditions (Oxy-biomass combustion) is one of the approaches achieving negative CO_2 emissions. KCl, K_2CO_3 and K_2SO_4, as the major potassium species in biomass ash, can catalytically affect biomass combustion. In this paper, the catalysis of the representative potassium salts on oxy-biomass combustion was studied using a thermogravimetric analyzer (TGA). Effects of potassium salt types (KCl, K_2CO_3 and K_2SO_4), loading concentrations (0, 1, 3, 5, 8 wt%), replacing N_2 by CO_2, and O_2 concentrations (5, 20, 30 vol%) on the catalysis degree were discussed. The comparison between TG-DTG curves of biomass combustion before and after water washing in both the 20%O_2/80%N_2 and 20%O_2/80%CO_2 atmospheres indicates that the water-soluble minerals in biomass play a role in promoting the devolatilization and accelerating the char-oxidation; and the replacement of N_2 by CO_2 inhibits the devolatilization and char-oxidation processes during oxy-biomass combustion. In the devolatilization stage, the catalysis degree of potassium monotonously increases with the increase of potassium salt loaded concentration. The catalysis degree order of the studied potassium salts is $K_2CO_3 > KCl > K_2SO_4$. In the char-oxidation stage, with the increase of loading concentration the three kinds of potassium salts present inconsistent change tendencies of the catalysis degree. In the studied loading concentrations from 0 to 8 wt%, there is an optimal loading concentration for KCl and K_2CO_3, at 3 and 5 wt%, respectively; while for K_2SO_4, the catalysis degree on char-oxidation monotonically increases with the loading potassium concentration. For most studied conditions, regardless of the potassium salt types or the loading concentrations or the combustion stages, the catalysis degree in the O_2/CO_2 atmosphere is stronger than that in the O_2/N_2 atmosphere. The catalysis degree is also affected by the O_2 concentrations, and the lowest catalysis degree is generally around 20 vol% O_2 concentration. The kinetic parameters under the different studied conditions are finally obtained.

1. Introduction

The awareness of the increase in greenhouse gas emission has resulted in the use of renewable energy and the development of new technologies that can accommodate capture and sequestration of carbon dioxide (Buhre et al., 2005; Ma et al., 2016). Biomass is considered as the CO_2-neutral fuel because it generates the same amount of CO_2 during combustion as is absorbed during growth through photosynthesis. In recent decades biomass is not only attracting interest to meet our growing energy demands, but is also facilitating our carbon reduction and renewable energy targets (Demirbas et al., 2009; Wang et al., 2013). Oxy-fuel combustion is a promising carbon capture technology for newly built and retrofitted coal-fired power plants based on the advantages of a relatively moderate efficiency penalty and the lowest retrofit capital expenditure (Chen et al., 2012; Li and Wei, 2013). Therefore, a combining technology which burns biomass under oxy-fuel combustion conditions, named "oxy-biomass combustion", can achieve "CO_2 negative emission" (Wang et al., 2014, 2015a).

There are a significant number of publications relating to alkali metal catalysts, especially potassium salts. However, the mechanisms of alkali metal catalysts are different in different research conditions. Among all the inorganic elements existed in biomass, potassium has the largest effect on catalyzing both biomass

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pyrolysis and gasification/combustion process as well as its thermal conversion characteristics. Several explanations for the catalytic role played by potassium have been proposed: (1) potassium can decrease the primary tar yield from decomposition and increase the gas and char products (Jensen et al., 1998; Jones et al., 2007); (2) potassium can enhance the soot oxidation by consuming the carbon to form carbonate species during soot combustion (Querini et al., 1999); (3) potassium can result in the lowest oxidation temperature, increase reaction rates of char combustion and bring higher conversion efficiencies (An and McGinn, 2006; Jones et al., 2007). Further, the potassium in the char is a good catalyst bringing higher conversion efficiencies in terms of carbon burn-out during char combustion process (Nowakowski et al., 2007). However, the high potassium content in biomass induces severe fouling and slagging in biomass-fired furnace (Wang et al., 2012; Ren and Li, 2015). One of the approaches to solve these problems in biomass combustion is to lower the potassium and chlorine contents in the biomass feedstocks (Wang et al., 2011). Water-leaching has proven highly effective at removing the minerals in agriculture biomass (Wang et al., 2015b). Deng et al. (2013) investigated the effect of water washing on biomass properties, and found that water washing removed 80–90 wt% potassium and relieved ash melting and fouling. However, the water washing also significantly affects the ignition and burnout characteristics of biomass, which indicates the catalysis of potassium on biomass combustion. In air atmosphere, although the catalysis of alkali and alkaline earth metals (AAEMs) on coal combustion and gasification have been widely reported (Backreedy et al., 2003; Nzihou et al., 2013; Quyn et al., 2002; Wagner and Mühlen, 1989), there are only few studies on the effect of the potassium catalysis on biomass combustion, especially in an O_2/CO_2 atmosphere.

The concept of oxy-fuel combustion is to remove the nitrogen from air and then to utilize flue gas recycle (mainly carbon dioxide and moisture) to proceed the combustion process in oxygen (Toftegaard et al., 2010). Based on the aspects of combustion chemistry, mass transfer and radiation heat transfer, the coal combustion process in oxy-combustion is expected different with that in traditional air combustion. CO_2 has a larger specific molar heat than N_2, and coal may be gasified by the CO_2, thus the use of CO_2 instead of N_2 causes a reduction in the particle surface temperature, flame propagation speed and stability of the flame as well as an increase in the unburned carbon content. These problems can be overcame by increasing the oxygen concentration in oxy-fuel combustion (Gil et al., 2012; Bejarano and Levendis, 2008; Zhou et al., 2016). In the past decade, quite a lot of investigations have been made to probe into different challenges associated with the ignition and burnout during oxy-fuel combustion. Under oxy-fuel combustion conditions, the combustion environment is significantly changed in oxygen concentration and temperature, depending on the combustion method types, thereby, the catalytic effects of AAEMs on the devolatilization and char-oxidation might be also affected. However, these catalytic effects of AAEMs on biomass combustion process in oxy-fuel combustion environment have not been reported in the present literatures.

This paper aims to investigate the catalysis effects of potassium on the devolatilization and the char-oxidation stages under air and oxy-biomass combustion conditions, and to seek if its catalytic influences are meaningful in these conditions. The effects of potassium salt types (KCl, K_2CO_3, and K_2SO_4), loading concentrations (0, 1, 3, 5, 8 wt%), replacing N_2 by CO_2, and O_2 volume concentrations (5, 20, 30 vol%) on the catalysis degree are studied in a thermogravimetric analysis (TGA) reactor.

2. Materials and methods

2.1. Material samples

The biomass used in this study is the wheat straw from Baoji district of Shaanxi province, China. Table 1 shows the proximate and ultimate analysis of raw wheat straw sample. The straw particles were pulverized and sieved into $\leq$200 μm.

To remove the minerals from the straw sample, the procedures of a hot water wash were applied. In the hot water wash, 10 g of straw were stirred in a beaker with 200 ml of deionized water at 80 °C for 6 h. After that, the water washed straw was filtrated, washed with 200 ml of deionized water and then dried in an oven at 80 °C for 24 h. Table 2 shows the ash composition analysis of both raw and water washed straw samples. From Table 2, after water washing, the content of potassium and sulfur in the ash decreased from 13.5% to 3.1%, and from 2.6% to 0.8%, respectively, and no chlorine was detected. Since the ash content was lowered by about half, the removing rates of K, Cl and S by water washing were 88.5, 100 and 84.6%, respectively.

In order to add potassium to the water washed straw sample, the three kinds of potassium salts including KCl, K_2CO_3 and K_2SO_4 were impregnated, respectively. For each kind of potassium salt, 0.005 g of potassium salt and 3 ml of deionized water were added into 0.495 g of the water washed straw in a glass beaker. The solution was thoroughly mixed for 12 h by a stirrer to make a distribution of the potassium salt uniform. After that, the mixed solution was dried for 24 h in an 80 °C oven. Thus, 1 wt% loading concentration of potassium salts including KCl, K_2CO_3 and K_2SO_4 in the water washed straw samples were obtained, respectively. In the resemble operation conditions, 3, 5 and 8 wt% potassium salts including KCl, K_2CO_3 and K_2SO_4 were impregnated, respectively. In this paper, the raw straw sample and the water washed straw sample are labeled as R_o and A_o, respectively. The serial numbers of samples with different loading potassium salt types (KCl, K_2CO_3 and K_2SO_4) and loading concentrations (1, 3, 5, 8 wt%) are shown in Table 3.

2.2. Thermogravimetric analysis methods

Thermogravimetric analysis was performed in a STA-409PC thermal analyzer (NETZSCH, German). 5 ± 0.1 mg of samples were loaded into an Al_2O_3 crucible for each run. In the experiments, the samples were carried out over a temperature range of 30–750 °C at a heating rate of 20 °C/min. The O_2 volume concentrations in the total carrier gas (O_2/N_2 or O_2/CO_2) flow of 100 ml/min were 5, 20 and 30 vol%, respectively. In TG and DTG curves, T_i is the ignition temperature (biomass volatile), °C; T_f is the burnout temperature (biomass char), °C; T_{peak1} is the temperature of the first peak in DTG curves (volatile release), °C; w_{max1} is the peak value of the first peak in DTG curves (volatile release), %/min; T_{peak2} is the temperature of the second peak in DTG curves (char-oxidation), °C; w_{max2} is the peak value of the second peak in DTG curves (char-oxidation), %/min.

3. Results and discussion

3.1. Effects of water washing and atmosphere on the biomass combustion

For the convenience of comparison under the varied conditions, T_i, T_f, T_{peak1}, w_{max1}, T_{peak2}, and w_{max2} of straw combustion under all the conditions are summarized in Table 4.

TG-DTG curves of straw combustion before and after water washing, in both $20\%O_2/80\%N_2$ and $20\%O_2/80\%CO_2$ atmospheres,