Catalytic behaviors of alkali metal salt involved in homogeneous volatile and heterogeneous char reforming in steam gasification of cellulose

Long Jiang[a], Changyi Liu[a], Song Hu[a,b,*], Yi Wang[a,b,*], Kai Xu[a], Sheng Su[a,b], Jun Xiang[a,b]

[a] State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China
[b] China-EU Institute for Clean and Renewable Energy at Huazhong University of Science and Technology, Wuhan 430074, China

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ABSTRACT

The current study aimed to investigate catalytic behaviors of alkali metal salt participating in homogeneous steam-volatile and heterogeneous steam-char reforming reactions in steam gasification of cellulose. The results indicate that the temperature is a key parameter which significantly influenced both yield and composition of gas and tar and catalytic performances of KCl. Externally added steam had negligible effect on cracking/reforming of macromolecules volatiles at the temperature of 700 and 900 °C without KCl, whereas in the presence of KCl, it would be activated and further reacted with low reactivity macromolecules volatiles, leading to an increase in gas yield and a decrease in tar yield. KCl was notably involved in homogeneous steam-volatile reactions, and enhanced the water gas shift reaction and tar reforming reactions. However, KCl had little promotion effect on thermal cracking/reforming of levoglucosan in homogeneous steam-volatile reforming process at 500 °C. Its inhibition effect on levoglucosan formation mainly acted during the primary pyrolysis reactions. KCl could also enhance heterogeneous in situ char-steam reaction resulting in a higher H_2 yield. The general pathway of KCl involved in homogeneous/heterogeneous reactions in steam gasification of biomass was eventually proposed.

1. Introduction

Nowadays, great efforts have been made to develop high efficient and advanced utilization routes of biomass. Gasification technology, especially steam gasification due to the high hydrogen production, has emerged as the most attractive one, wherein, biomass reacts with an active gasification agent to be converted to fuel gas for gas turbines/engines, fuel cell, etc. or feedstock gas for synthesis [1,2]. Accordingly, the fundamental knowledge of the reaction mechanisms and processes has been broadly researched and developed toward various aspects [3–7]. Among those aspects, ash-forming mineral in biomass feedstock is considered as an important topic in biomass gasification. In contrast to the traditional fossil fuels such as petroleum and coal, one of the significant features of woody biomass is in the presence of considerable content of alkali and alkaline earth metallic species (AAEMs) such as potassium, sodium, calcium, and magnesium [8–10], which are the indispensable integral nutrient constituents in plant growing process. Those metallic species are the major composition of ash-forming mineral in woody biomass, whose content is generally less than 1 wt% [2,6]. However, the content of AAEMs is up to 5 wt% in some

herbaceous and forestry biomass [11].

In view of the high content of AAEMs which are thermally unstable, a considerable part of them is prone to be volatilized in gaseous form [12–14] which will bring two major issues in biomass gasification process. On the one hand, they will lead to agglomeration/slagging in gasifier chamber, as well as ash deposition and hot corrosion on the downstream heat exchangers [15,16], resulting in efficiency reduction as well as extra operation and maintenance cost of gasification system. On the other hand, AAEMs will bring catalytic effect on biomass thermal conversion [17–20], thereby altering reaction routes of gasification. As is well-known, biomass gasification includes two main processes: thermal decomposition and consequent volatile/char reforming. It has been reported that once decomposition of biomass occurs, a small amount of AAEMs are released, and a pronounced release of AAEMs is observed at the temperature over 500 °C [21–23]. The released AAEMs will be further involved in the consequent homogeneous volatile reforming or heterogeneous char reforming reactions. Accordingly, gasification process should be changed significantly via homogeneous/heterogeneous catalytic alteration of those reaction pathways by AAEMs. Thus, a well understanding of catalytic behaviors of AAEMs

participating in homogeneous volatile and heterogeneous char reforming reactions in gasification process is essential for deeply revealing gasification mechanism of biomass. Many works [17–20,24,25] have been reported on the catalytic effect of AAEMs in biomass pyrolysis/gasification process. Wang et al. [17] investigated the effect of both naturally occurring and externally added AAEMs during catalytic pyrolysis of biomass and found that both of them impacted product distribution. AAEMs could decrease hydrocarbon yields and enhance cracking and dehydration reactions of hydrocarbons increasing thermally-derived COx, and their effect followed the order: K > Na > Ca > Mg. Similar results about lowering onset temperature of pyrolysis and char gasification [18], as well as increasing in the yield of char and gas at the expense of bio-oil [19,20] have been reported. Our previously published works [24,25] also found that the naturally occurring AAEMs exhibited a significant catalytic role in thermal cracking/reforming of producing tar, enhancing the hydrogen yield. However, studies on distinguishing the homogeneous and heterogeneous catalytic behaviors of AAEMs in biomass gasification could hardly be found in the open literature.

The alkali metal of potassium has highest reactivity and largest content in most types of biomass [11,26], so it is believed to be playing a dominant catalytic role in above gasification reactions [27]. Moreover, releasing mechanism of potassium during biomass pyrolysis/gasification has also been well revealed that potassium is released predominantly in the form of KCl [28–30]. Therefore, the recent work aimed to investigate catalytic behaviors of KCl separately involved in homogeneous steam-volatile and heterogeneous steam-char reforming reactions to further understand the homogeneous/heterogeneous catalytic mechanism of AAEMs in steam gasification of biomass.

Cellulose, as a major biomass component (its share is generally 40–60 wt% in plant biomass [31] and can even reach 80–95 wt% in cotton, ramie, flax and chemical pulp [32]), is the most abundant natural and renewable polymer on earth, whose annual production by photosynthesis in the world is estimated to be 10^{11}–10^{12} ton [33]. The results of previous studies [34–38] indicate that the overall rate of biomass pyrolysis as well as the production of global volatiles (including non-condensable gases) and char corresponded to the summation of the individual contributions from the three major components. Furthermore, cellulose, rather than other biomass feedstock, is ash-free that can totally avoid interference brought from inherent AAEMs in thermochemical reactions. Therefore, cellulose was chosen as a representative compound of biomass using in current study.

In this study, thermal decomposition and consequent volatile/char reforming of cellulose were implemented in a dual-stage quartz reactor. Yield and composition of gaseous product were obtained by using a gas chromatography (GC). Lighter composition and whole aromatic ring structure of tar were analyzed respectively using gas chromatography–mass spectrometry (GC–MS) and ultraviolet fluorescence spectroscopy (UV-Fs). Based on those data, the catalytic mechanism of KCl separately involved in homogeneous steam-volatile and heterogeneous steam-char reforming reactions was discussed.

2. Experimental

2.1. Materials

Powder of α-cellulose (purchased from Sigma Aldrich Company, product No. C8002) was sieved and the particles with diameter between 125 and 210 μm were selected and air-dried in an oven at a temperature of 80 °C for 24 h used for this study. Results of the proximate and ultimate analysis (respectively measured by TGA-2000 (Las Navas Instruments, Spain) and EL-2 analyzer (Vario Company, Germany)) are presented in Table 1.

2.2. Experimental setup and procedure

Steam reforming of cellulose was conducted using a lab-scale dual-stage quartz reactor. The experimental system mainly included a gas supply unit, a gas carrying feeding unit, a high performance liquid chromatography (HPLC) pumping unit (feeding different concentration of KCl solution), a dual-stage quartz reactor, a tar condenser and capture unit as well as a gas drying and monitor unit as shown in Fig. 1. The dual-stage reactor, which was heated in a temperature programmed tube furnace, was divided into two parts by quartz sieves (mesh diameter of the upper sieve is 200 μm, and that of the other two below is 100 μm). The bottom reactor (inner diameter of 40 mm and length of 80 mm), which was integrated with the sample feeding unit and the HPLC pumping line, was fluidised using acid washed and calcined silica sand (particle size of 83–150 μm). This part was used as a pyrolyzing and heterogeneous in situ steam-char reforming reactor. The upper reactor (inner diameter of 40 mm and length of 120 mm) also integrated with another HPLC pumping line was used as a homogeneous steam-volatile reforming reactor. The upper section out of the furnace were heated at 180 °C by a heating tape to avoid any condensation of semi-volatile substances (unreacted steam, tar, etc.).

2.2.1. Homogeneous steam-volatile reforming

Before each experiment, all the reactor and gas tubes were flushed by nitrogen gas (purity > 99.999%) to remove impurities from the system. The nitrogen flow was separated into two channels. One's inlet from the bottom of reactor (flow rate of 0.7 L/min) was used as a fluidizing gas. The other one installed a piezometer was used as a carrier gas of cellulose powder feeder (flow rate of 1.0 L/min). When the reactor was heated and stabilized at the desired temperature, the upper HPLC pumping line was running to feed different concentration of KCl solution (0.1 ml/min, steam flow: ca. 125 ml/min, KCl reagent grade is analytically pure). Then the cellulose powder was carried into the fluidized reactor at the rate of 0.1 ± 0.02 g/min by the feeder via a water cooled concentric tube, wherein, it was pyrolyzed at a high heating rate to ensure fast devolatilization. The cellulose feeding time was lasted for 10 min. The resulting volatile consequently flowed into the upper reactor, wherein, it was reformed by steam with different concentration of KCl. After reforming, the gas flow successively passed through four tar traps to capture tars, whose method and tar yield determination have been described elsewhere [24]. Briefly, four tar traps were loaded with 0, 50, 50 and 30 ml of HPLC-grade chloroform and methanol mixtures (volume of 4:1, chromatographically pure, purchased from Sinopharm chemical reagent Co., Ltd, Shanghai). The former two traps were ice salt water cooled (0 °C) to condense the unreacted steam and parts of heavier tar. The latter two were dry ice cooled (−78.5 °C) to ensure capture of the rest tars. Tar-free flow was dried by anhydrous calcium chloride and cotton wool filter. Its composition was analyzed by a gas analyzer (Gasboard-3100, Wuhan Cubic Optoelectronics Co., Ltd., China). Then the clean gas was totally sampled using a 25 L gas collector which was analyzed by a GC. The calculation method of gas yield has been also described in our previous work [24]:

$$Hydrogen\ yield = \frac{flow\ rate\ of\ nitrogen \times collection\ time}{concentration\ of\ nitrogen}$$
$$\times \frac{concentration\ of\ hydrogen}{weight\ of\ feeding\ biomass} \times \frac{1000}{22.4}\ mmol/g \quad (1)$$

where concentration of hydrogen and nitrogen was determined from the gas collector by using GC. Similarly, other yields of gases could be also calculated by the equation.

In the end, the fresher mixture solvent in the latter two traps was used to wash pipelines and traps, and the total solvent was well mixed, accurately weighed and collected in a brown bottle which was stored in a freezer used for further analysis. Yield of tar was measured by a