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Evolution of char structural features during fast pyrolysis of corn straw with solid heat carriers in a novel V-shaped down tube reactor

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ABSTRACT

Investigating structural properties of the chars derived from biomass pyrolysis and their evolution mechanisms is of potential interest because they play crucial roles not only in biomass thermochemical conversion but also for bio-char processing and high value-added utilization. In this study, the evolution of char structural features during fast pyrolysis of corn straw with solid heat carriers in a novel V-shaped down tube reactor was studied within a wide temperature range of 200–900 °C. The char fractal properties were explored to evaluate the complexities of pore development. In addition, the volatilization behaviors of the alkali and alkaline earth metallic species (AAEMs) during rapid pyrolysis were analyzed in detailed. The H/C and O/C ratios were reduced by 85.5% and 89.8% respectively in response to increasing temperature until 900 °C. Great loss of O-containing structures, particularly ether and C=O groups, resulted in more aromatic and ordered structure of the chars at high temperature. The evolution of pore structure exhibited a three-stage development. Increasing temperature gave rise to progressive increase in porosity development, whereas the maximum BET surface area and pore volume appeared at 500 °C. The pore fractal dimension (D_s) and BET surface area (S_{BET}) demonstrated an excellent positive linear correlation. The volatilization extent of AAEMs significantly depended on temperature in the order of Na > K > Mg > Ca. The K and Na concentration in chars reached maxima of 1.123 wt% and 0.049 wt% at 350 °C, respectively.

1. Introduction

Nowadays, the development and utilization of biomass have aroused widespread interest, as it is considered as the only carbon-containing renewable potential source of fuels and chemical feedstocks [1]. In China, agricultural crop residues are the most abundant biomass resource with the annual output of over 800 million tons [2] and increasingly recognized as the future feedstocks that will enable sustainable bioenergy production. At present, corn straw, as a kind of typical agricultural waste, is produced with the annual output of 216 million tons in China [3].

In this situation, there is an urgent need to develop advanced and environmentally friendly technologies for the clean and efficient utilization of agricultural waste, in which pyrolysis constitutes an attractive option [4], since it provides a high adaptability in utilizing a variety of feedstocks and versatile application of pyrolysis products including biofuels, chemicals, heat, power, etc [5]. Moreover, pyrolysis is recognized as the important first step in most biomass thermochemical conversion processes such as gasification and combustion [6,7], which has significant effects on the subsequent char conversion and products distribution [8]. The pyrolysis products can be categorized into three fractions, i.e., gas, bio-oil and char [9]. The evolution mechanisms of main gaseous pyrolysates have been discussed thoroughly in our previous publications [10,11]. The char structural evolution characteristics also play crucial roles in biomass conversion processes. It is well established that the surface morphology and physico-chemical structure of biomass particles can undergo drastic changes with the violent release of volatiles during fast pyrolysis. The derived char is highly heterogeneous and reactive. The change of internal structure of char particles not only affects their physical properties (i.e., mechanical, transport and adsorption properties) but also largely determines char reactivity and thus char conversion [12,13]. Moreover, the char structure also influences the physico-chemical speciation and dispersion of intrinsic alkali and alkaline earth metal species (AAEMs) as inherent catalysts [14,15], which have an obvious impact on their catalytic activity. In addition, the char structure has obvious influence on the formation of ash and pollutants. Therefore, it is important to elucidate the structural properties of the derived chars and the evolution

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mechanisms during pyrolysis, especially for rapid heating rates commonly employed during the industrial thermochemical conversion.

Directly heating of biomass with high temperature heat carriers to achieve rapid pyrolysis without carrier gases introduced is a promising pyrolysis technology that has aroused the concern and interest of many researchers. The novel V-shaped down tube (VDT) reactor developed by our research group has been proven to be suitable for biomass fast pyrolysis achieved by rapidly mixing the cold or preheated biomass feedstocks with hot ceramic ball heat carriers [16,17]. Compared to the commonly used fluidized beds, the VDT reactor exhibits different characteristics. Direct heating of biomass particles by heat carriers achieve fast pyrolysis without carrier gases introduced and their vigorous movement ensures good mixing and contact, as well as effective heat transfer. The reactor internal stable negative pressure environment allows operating with short volatile residence times. Since large amounts of carrier gases are not required, the subsequent pyrolysis vapors cooling energy consumption is greatly decreased, and the volume of the bio-oil recovery system is reduced accordingly. It is worth noting that the aforementioned reactor features are crucial for improving pyrolysis efficiency, improving bio-oil yield and reducing energy consumption. To date, studies on biomass pyrolysis have mainly been carried out under different carrier gas atmospheres [18–21], mainly focusing on the effect of different pyrolysis factors on the structural characteristics of biomass chars [22–25]. It has been reported that the carrier gas atmospheres have an impact on the characteristics of pyrolysis products [18]. Unfortunately, there is still little detailed information on the evolution of pryolysis char structural features without carrier gas atmospheres, especially for fast pyrolysis in a V-shaped down tube reactor. The effect of ceramic balls in the novel V shaped reactor tube mainly involves three aspects. First, as fast pyrolysis of biomass is achieved by rapidly mixing the feedstocks with high-temperature ceramic ball heat carriers, the heat transfer between them exerts significant influence on the pyrolysis behaviors of biomass, therefore affecting the resulting char structural characteristics. Secondly, the mutual collision between them is inevitable during their contact heat transfer process, which could have an impact on the surface morphology of the char particles. Finally, as the used ceramic ball mainly contains silica and alumina, it has a catalytic effect on the pyrolysis of biomass, which in turn affects the char structure development. Investigating char structural evolution of features during fast pyrolysis of biomass with solid heat carriers is important for further in-depth understanding the pyrolysis behaviors. This aspect remains a topic of interest to be explored.

In this study, the evolution of char structural features without carrier gas atmosphere during fast pyrolysis of corn straw in a novel V-shaped down tube reactor was studied within a wide temperature range of 200–900 °C. The char fractal properties were explored to evaluate the complexities of pore development. In addition, the release characteristics of the AAEMs during fast pyrolysis was analyzed in detailed. Further improved understanding about the above subjects is important for better insights into char structural evolution during fast pyrolysis of biomass in a V-shaped down tube reactor, which provides the basis for biomass effective thermochemical conversion and high-valued utilization of bio-char.

2. Material and methods

2.1. Raw materials

Corn straw (CS), as a kind of typical Chinese agricultural waste, was used as feedstock for fast pyrolysis. The sample was air-dried, crushed and sieved to a particle size smaller than 1.5 mm. The proximate and ultimate analysis of biomass samples were performed using a STA 449 thermogravimetric analyzer (TGA, Netzsch, Germany) and in an EuroVector Euro EA 3000 elemental analyzer, respectively. The higher heating values (HHVs) were measured in a C2000 bomb calorimeter (IKA, Germany). Table 1 presents its main properties. The temperature and corrosion resistant alumina ceramic balls with a diameter of 2–3 mm were used as heat carriers. Their bulk density was approximately 2200 kg/m^3 and the specific heat capacity was 840 J/(kg·°C). The ceramic balls showed negligible wear and their weight change was found to be below 5% after 500 h of operation time.

Table 1
The main properties of corn straw.

Properties	Corn straw
Proximate analysis[a] *(wt.%)*	
Moisture	6.27
Volatile matter	75.29
Fixed carbon	12.46
Ash	5.98
Ultimate analysis[b] *(wt.%)*	
Carbon	47.32
Hydrogen	6.27
Nitrogen	1.02
Oxygen (by difference)	45.39
Micropore volume (cm^3/g)	0.74×10^{-3}
Mesopore volume (cm^3/g)	2.18×10^{-3}
Total pore volume (cm^3/g)	8.59×10^{-3}
BET surface area (m^2/g)	1.57
HHV (MJ/kg)	16.79

[a] As received basis.
[b] Dry and ash free basis.

2.2. Pyrolysis experimental setup and procedure

The continuous V-shaped down tube pyrolysis system used for corn straw fast pyrolysis was shown in Fig. 1, which mainly consisted of a V-shaped down tube reactor, a biomass feeding system, a heat carrier heater, a gas-solid separator, two diffusion cyclones, a bucket elevator, a bio–oil recovery system. The essential design characteristic was the circulation of hot ceramic balls as heat carriers in a closed loop, which supplied the heat required for fast pyrolysis by rapidly mixing the cold or preheated biomass feedstocks with hot ceramic balls in the reactor. The feeding system was composed of a cylindrical vessel, a plough type scraper quantitative feeder equipped with a vertical shaft connected to a plough type scraper and a horizontal screw feeder. The V-shaped down tube reactor was the heart of the pyrolysis system. The developed down tube was V-shaped, the reaction tube diameter of 89 mm, pipe wall thickness of 6 mm, two-stage reaction tube included angle of 90°, the total length of 2.4 m. The bio–oil recovery system mainly included a spray condenser, a bio-oil filter, an oil pump, a plate heat exchanger, a bio-oil storage tank.

Prior to the pyrolysis runs, the heat carrier loop consisting of the down tube reactor, the bucket elevator and the heat carrier heater was first preheated by circulating ceramic balls heated in the heat carrier heater until the thermal insulation of heat carrier loop was approximately in thermal equilibrium. After this period, the equipment could be kept in steady-state conditions and ready to start pyrolysis experiments. According to our preliminary tests, the most reliable operation and maximum availability and throughput of the pyrolysis liquefaction system were obtained by using a heat carrier-to-biomass mass ratio of approximately 20, which ensured their efficient mutual contact for high heat transfer rate and bed isothermality. The subsequent studies were confined to this ratio.

In each run, approximately 100 kg of biomass feedstock was stored in a closed storage vessel at a feed rate of 5 kg/h continuously fed to the pyrolysis unit, allowing continuous operation for a long time to determine reliable mass and energy balances within the limits of reproducibility. The ceramic balls were heated to the desired temperature in the heat carrier heater and then subsequently brought into the VDT reactor at a constant cycle rate of 100 kg/h. After the reactor