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The effect of temperature and heating rate on char properties obtained from solar pyrolysis of beech wood

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HIGHLIGHTS

- Char was obtained during solar pyrolysis at various temperatures and heating rates.
- "Solar chars" up to 2000 °C and up to 450 °C/s have been produced.
- Temperature and heating rate jointly affected char yield, structure and reactivity.
- Reactivity evolution with temperature and heating rate were related to structure.

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ABSTRACT

Char samples were produced from pyrolysis in a lab-scale solar reactor. The pyrolysis of beech wood was carried out at temperatures ranging from 600 to 2000 °C, with heating rates from 5 to 450 °C/s. CHNS, scanning electron microscopy analysis, X-ray diffractometry, Brunauer–Emmett–Teller adsorption were employed to investigate the effect of temperature and heating rate on char composition and structure. The results indicated that char structure was more and more ordered with temperature increase and heating rate decrease (higher than 50 °C/s). The surface area and pore volume firstly increased with temperature and reached maximum at 1200 °C then reduced significantly at 2000 °C. Besides, they firstly increased with heating rate and then decreased slightly at heating rate of 450 °C/s when final temperature was no lower than 1200 °C. Char reactivity measured by TGA analysis was found to correlate with the evolution of char surface area and pore volume with temperature and heating rate.

1. Introduction

Biomass is a renewable energy source that can partly relieve the energy crisis and environmental problems. Then the technology converting biomass effectively and efficiently into fuel and chemical stock receives more and more attention. Pyrolysis is one of the most attractive processes to convert biomass into economically renewable intermediates (Mettler et al., 2012). As pyrolysis is an endothermic thermochemical process, external heat is required. In standard pyrolysis, the heat is obtained by combustion of fossil fuel or of part of the initial biomass, which reduces the energy efficiency and increases the pollution discharge (Nzihou et al., 2012). For avoiding the disadvantage of standard pyrolysis, concentrated solar energy can be used to provide the heat for pyrolysis reactions. The biomass directly absorbs the heat from concentrated solar energy thus resulting in fast or rapid pyrolysis, producing gases, tar and char.

The char is carbon-rich and can be further used as a fuel (gasification and combustion) or decontamination adsorbent. Firstly, it is necessary to understand the char reactivity for designing a high efficiency gasification or combustion reactor (Cetin et al., 2005). Secondly, the appropriate pore structure and surface area are important for preparing decontamination adsorbent (Demirbas et al., 2006). For making better use of char obtained from solar pyrolysis, the composition, surface area, pore structure and reactivity should be investigated in advance. Char reactivity and morphological structure are especially affected by the pyrolysis conditions (Blasi, 2009; Raveendran and Ganesh, 1998). The effects of pyrolysis conditions on the structure and reactivity of biomass chars have been investigated in several studies in relation to the following parameters: temperature (Fu et al., 2012a, 2011; Kim et al., 2012; Min et al., 2011; Bonelli et al., 2001), heating rate (Mermoud et al., 2006; Guerrero et al., 2005; Fushimi et al., 2003), residence time and pressure (Cetin et al., 2005, 2004).

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The char carbon content increases with temperature, which is the indication of increased structure ordering for lowering the reaction site concentration (Kumar and Gupta, 1994). The char surface area increases with temperature and then slightly decreases when the temperature is higher than 1173 K (Fu et al., 2012b). There is a significant diminution in char reactivity with the increase of temperature (above 1073 K) as previously reported (Guerrero et al., 2005; Chen et al., 1997). At lower temperature (below 1073 K), the release of volatile intensifies owing to the temperature increase enlarges the char surface area. However, there are more and more structural ordering and micropore coalescence for char when temperature keeps on increasing even higher than 1073 K.

The increase of heating rate causes a weak decrease in the carbon content and an increase in hydrogen and oxygen content of char. Moreover, the heating rate effect tends to disappear at high temperatures (Antal and Grønli, 2003). The presence of higher hydrogen and oxygen contents is related to the availability of active sites and thus to enhanced reactivity (Laurendeau, 2009). For slow heating rates (lower than 1 °C/s), no major change takes place in the particle morphology as volatile is released through the natural porosity (Della Rocca et al., 1999). For fast heating rates (higher than 10 °C/s), the original cellular structure is lost as a consequence of melting (Kurosaki et al., 2003). When the heating rate increases, the volatile release speeds up. Then large internal cavities and a more open structure of char is produced (Guerrero et al., 2005) owing to the fast volatile release producing internal overpressure and coalescence of the smaller pores, which leads to the increase of surface area and pore volume. So the char reactivity increases with heating rate can be explained by the higher surface area and pore volume (Cetin et al., 2005, 2004). Besides, heating rate rising shortens tar vapors residence time in pores and reduces the condensation reaction leading to char reactivity increase (Kurosaki et al., 2003). However, char obtained at high heating rate has lower surface area compared to that at low heating rate when temperature was 900 °C (Fu et al., 2012b). It is attributed to too high heating rate causing char interior higher temperature, a partial graphitization with formation of grapheme structure occurs, which does not contribute to the development of large surface area.

Almost all of the above conclusions have been deduced from univariable analysis. However, there is little information on the char prepared at different pyrolysis temperatures with different heating rates (Angin, 2013; Fu et al., 2012b). In this study, the bivariate analysis was used for investigating the combined effect of pyrolysis temperature and heating rate on char characteristics. Besides, there are two characteristics for the solar reactor that may affect char characteristics: (1) High temperature and heating rate can be achieved; (2) Two temperature zones exist as described in Ref. Hopkins et al. (1984) and modeled in Ref. Zeng et al. (2014a). Indeed, since only the sample is directly heated by solar radiation, the "hot" sample is surrounded by relatively "cold" gas. Then, most vapors issued from primary reactions are quenched as soon as they leave the sample. Then the evaluation of char obtained in two temperature zones reactor at high temperature (up to 2000 °C) and high heating rate (up to 450 °C/s) is investigated for the first time. The purpose of this paper was to: (i) characterize the structure and composition of chars generated under different pyrolysis conditions; (ii) study the reactivity of char prepared at different temperatures and heating rates; (iii) relate the characterization and reactivity for the char.

2. Experimental

2.1. Materials

Beech wood pellets were used for pyrolysis experiments. The initial sawdust particle size ranged from 0.35 to 0.80 mm. After sawdust compaction, the pellets were cylinders with 10 mm in diameter and 5 mm thick. The proximate analysis of beech wood is 85.3% volatile matter, 14.3% fixed carbon, 0.4% ash and 6% moisture. The ultimate analysis for beech wood is as follows: C = 50.8%, H = 5.9%, O = 42.9%, N = 0.3% and S = 0.02%.

2.2. Pyrolysis experiments

2.2.1. Solar reactor

As shown in Fig. 1, pyrolysis experiments were carried out under an argon flow in a transparent Pyrex balloon reactor (inside

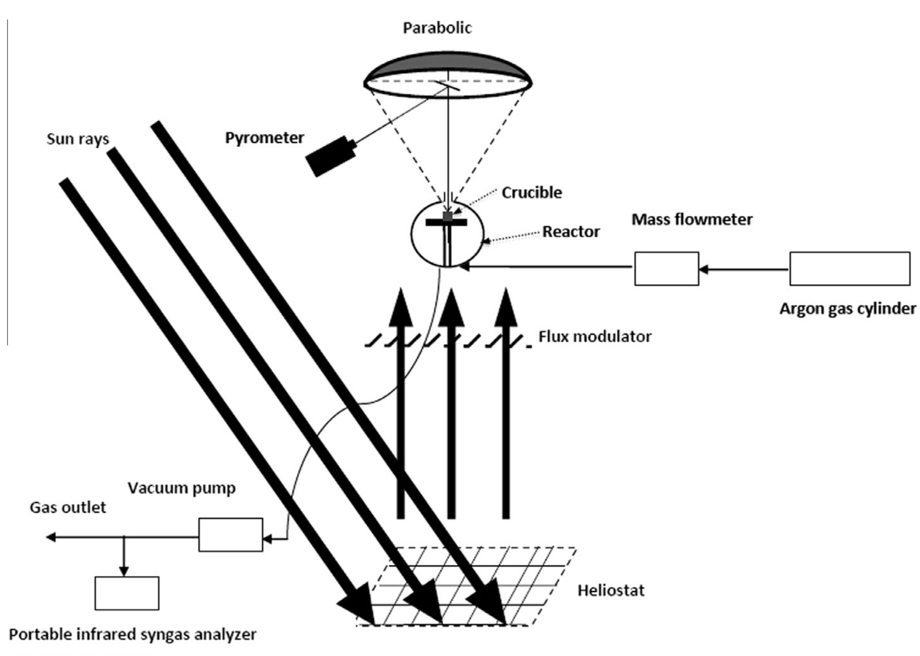

Fig. 1. Schematic of the solar pyrolysis experimental setup.