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Research Paper

Experimental research of basic properties and reactivity of waste derived chars

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HIGHLIGHTS

- Physical and chemical properties of RDF char and BDF char were studied.
- Activation energy and reaction heat of combustion and gasification were calculated.
- BDF ash showed improved catalytic activity compared to RDF ash.
- Catalytic activity became weaker due to the evaporation AAEM species.

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ABSTRACT

Two types of waste derived chars were prepared by pyrolyzing at 600 °C biomass derived fuel (BDF) produced from rice straw and refuse derived fuel (RDF) composed of municipal solid waste and sewage sludge. Thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) were used to investigate the non-isothermal combustion and gasification of the two chars. Kinetic study and reaction heat analysis were carried out and the results were compared. The chemical composition, internal structure, surface condition and carbon structure were also characterized to help understand the basic properties of waste derived chars and its relationship with the reactivity. The results showed that the BDF char samples were more porous and active than the RDF char samples. The total surface area of the BDF char samples was 209.7 m^2/g and the percent of micropore was over 90%. But the surface area and percent of micropore for the RDF char samples were significantly lower. The relative content of graphitic carbon was 54.4% for the RDF char and 72.5% for the BDF char samples, indicating a more ordered carbon structure of the BDF char. The activation energies under combustion and gasification conditions were 50.1 $kJ\ mol^{-1}$ and 137.9 $kJ\ mol^{-1}$ for the RDF char, and 36.6 $kJ\ mol^{-1}$ and 119.5 $kJ\ mol^{-1}$ for the BDF char, respectively, as calculated by Ozawa–Flynn–Wall method. The ash of the BDF char samples showed improved catalytic activity compared to the RDF char samples. However, the catalytic activity was weaker for the gasification process due to the evaporation of AAEM (alkali and alkaline earth metals) species at high temperatures, especially potassium.

1. Introduction

The recycling and safe treatment of municipal solid waste (MSW) materials have become a global challenge, especially for the developing countries, where MSW typically has high moisture content (up to 50–60%) and subsequently low calorific value (4–5 MJ/kg). The processing of MSW before further utilization is very popular, especially in Europe, in specific streams like Materials Recovery Facilities (MRFs) or Mechanical Biological Treatment (MBT) plants. MRFs and MBTs process MSW for the extraction of recyclables, such as metals, plastics and glass, and the improvement of the MSW for further treatment. These facilities typically produce a Refuse Derived Fuel (RDF) with a significantly higher calorific value than the initial MSW. This is associated with the removal of the moisture, the production of a more homogeneous feedstock-size and, in some cases, the selection of waste materials with specific properties, i.e. calorific value, moisture content, chlorine content, etc. [1,2].

Another big problem of the fast-growing world is the sewage sludge, defined as the residual, semi-solid material that is produced as a by-product during sewage treatment of industrial or

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municipal wastewater [3]. In some cases, sewage sludge is co-combusted with MSW or RDF in waste to energy (WTE) plants [4]. However, sewage sludge has low calorific value (4–5 MJ/kg), and therefore, the efficiency of the WTE facilities is significantly reduced. Also, MSW and RDF contain chlorine mainly associated with the plastics and other solid materials, which sometimes makes the mass burn in conventional WTE facilities challenging, since chlorine is linked with the formation of dioxins and furans during combustion and the erosion and corrosion of the superheaters and boilers.

Biomass derived fuels (BDFs) are fuels derived from plant-based or lignocellulosic biomass materials that are not used for food or feed. Biomass can be combusted to produce heat, or processed for the conversion into various forms of biofuel. Processing involves: thermal, chemical, and biochemical methods. However, simpler methods are also applied, such as drying of the plant feedstock, crushing of the biomass material to an appropriate size and compression of the product for the production of pellets.

Recent developments introduce thermal treatment of waste materials in gasification or pyrolysis processes, with little or no air, accordingly, at lower temperatures than full combustion, to produce syngas, which is a high calorific fuel and can be used in various applications, such as fuel for heat and power generation plants, transportation fuel, chemicals and others [5,6]. The main challenges of these processes are the tar removal from the syngas produced, which is directly related with the thermal efficiency of the syngas; and the beneficial use of the char produced, which is the main by-product of these processes [7,8].

The char yield is directly proportional to the feedstock used for pyrolysis, and typically, for biomass materials varies between 20% and 40%. Char can be efficiently used for soil improvement applications, since it indicates high water absorptivity and therefore, can effectively keep the moisture of the soil at an optimum level [9]. However, char is a carbonaceous material with a high calorific value, which in some cases it can be as high as 32 MJ/kg. Therefore, it can be used as a fuel in power plants for energy and heat generation or as a feedstock in gasification plants to produce H_2 and CO. A typical down-draft' gasification process involves four processing stages: drying of the feedstock to remove moisture; pyrolysis at 250–550 °C for the removal of volatiles and the production of char; reaction of the volatiles and char with oxygen to primarily form carbon dioxide and small amounts of carbon monoxide, which provides heat for the subsequent gasification; and, gasification process occurs as the char reacts with steam and carbon dioxide to produce carbon monoxide and hydrogen. Char gasification is a very promising management method associated with the relatively low reaction rate, high calorific and high porous carbonaceous structure that char materials indicate and the subsequent production of high amount of energy, less amount of tar and high quality syngas [10].

The combustion and gasification reactivity of char can be affected by many factors, such as the carbon structure, total surface area, ash content and preparation method. Bouraoui et al. [11] studied the effects of textural, structural and chemical properties of five lignocellulosic chars on the gasification rate with 20% CO_2 in nitrogen at 800 °C. The gasification rate was shown to depend on the char external surface, the potassium content and the D_3/G Raman ratio, up to 70% of conversion. At a higher conversion ratio, a satisfactory correlation between the Catalytic Index and the average gasification rate was identified. The catalytic index was defined as the ratio of the sum of the inorganic elements with catalytic potential (K, Ca, Mg, Na, Fe) to the sum of the inorganic elements with inhibiting effect (Si, Al). Xiao et al. [12] investigated the effects of particle size, pyrolysis temperature and pyrolysis atmosphere on the kinetics characteristics of straw semi-char gasification with CO_2. The results showed that a smaller particle size enhanced the conversion rate and gasification reactivity of semi-chars. Also, the gasification reactivity of semi-chars increased with pyrolysis temperature and reached its maximum at approximately 400 °C. Experiments were also conducted under H_2 and showed improved reactivity compared to char samples prepared under CO_2. Jayaraman et al. [13] analyzed thermogravimetrically char, produced from high ash Indian coal. He observed that gasification of the samples was affected by operating conditions such as reaction temperature, char production method, and particle size in addition to the chemical composition and the physical structure of the char. Qin et al. [14] studied the relationship between the chemical composition and the combustion reactivity of wood, straw and bark char samples. The main finding was that straw char was more reactive due to the high ash content of the straw, which was especially rich in potassium. There are many studies associated with the combustion and gasification of various materials under different conditions. However, the interconnection between the physical and chemical properties and the reactivity of char samples has not been adequately addressed.

The aim of this study was to characterize the kinetic behavior and reaction heat of two waste derived chars, RDF char and BDF char, under various combustion and gasification conditions. Thermogravimetric analysis was used and the activation energy was calculated by the Ozawa–Flynn–Wall and Vyazovkin methods. The chemical and microstructural properties and, the surface condition and carbon structure of the char samples were also characterized to help understand the basic properties of chars and the relationship with the reactivity.

2. Experimental and analytical methods

2.1. Char samples preparation

The RDF and BDF were provided by Hangzhou Jinjiang Group, China and Zhejiang Zhongyuan electrical packaged technology co., LTD, China, respectively. The materials and preparation methods used in this research are presented in Fig. 1. RDF was produced from a mixture of sewage sludge (70 wt.%) and processed MSW (30 wt.%). The mixture was processed with aerobic bacteria to remove moisture and sorted in different fractions to remove recyclable-incombustible materials. BDF was made of rice straw which is abundant in the rural area of China. BDF samples were produced by natural drying of the rice straw to a moisture content of about 10 wt.%, crushing of the biomass feedstock to reduce the particle size and compression of the produced material. The RDF and BDF were cylindrical with a diameter of 5 mm and a length of 5–20 mm. Char samples were produced in a laboratory muffle furnace at 600 °C for 1 h under N_2 atmosphere. Raw chars were sieved to particle sizes of less than 150 μm and kept in dry atmosphere before testing.

2.2. Char samples characterization

Ultimate and proximate analyses of char samples were measured by Carbon-Hydrogen-Nitrogen analysis (5E Series-CHN2000 Ultimate Analyzer) and by thermogravimetric analysis (5E Series-MAG6700 Proximate Analyzer), respectively. X-ray fluorescence (XRF, ARL ADVANT'X IntelliPower Series 4200) analysis was used to characterize the composition of the RDF and BDF ash samples. The results are reported as oxides.

The surface area and porosity of char samples were analyzed by a micropore adsorption instrument (ASAP 2020M Plus Physisorption). The temperature for gas removal was 250 °C. Gas adsorption measurements were performed at −196 °C. The total surface area was determined by the Brunauer-Emmett-Teller (BET) method on a model of adsorption which incorporates multilayer coverage.