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Comparative study of characterization and utilization of corncob ashes from gasification process and combustion process

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HIGHLIGHTS

- Basic properties of CCA from gasification and combustion process were investigated.
- Gasification CCA has a higher content of nutrient elements than combustion ashes.
- The agglomeration tendency of biomass ash could be enhanced at high temperatures.
- Combustion CCA is more suitable for use as a pozzolan source than gasification CCA.

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ABSTRACT

In the present study, fly ashes were obtained as a byproduct respectively from the processing of corncob in a gasification plant and from the combustion of corncob in a muffle furnace. The aim of this study is to characterize the basic properties of the fly ashes from gasification process and combustion process whilst comparing the results between these two types of solid residues to evaluate their potential applications. The results indicate that the CCA from gasification is more suitable to be used as a raw material for activated carbon owing to its larger specific surface area and higher carbon content compared with the CCA from combustion. With higher concentrations of K, Ca, and P, the CCA from gasification process is more bioavailable than CCA from combustion to be soil amendment. SEM images show that these CCA particles are agglomerated and irregular in shapes. The external surface of agglomerated particles is covered with potassium chloride. The influence of ashing temperature on ash morphology and agglomeration behavior is obvious, and the agglomeration tendency and melting degree are enhanced at high temperatures. Thermal analysis reveals the stepwise mechanism of decomposition for CCA. Specifically, the combustion CCA is more suitable for use as a pozzolan in blended cement concrete compared with the gasification CCA. Also, all ash samples with high silica content are suitable for ceramics.

1. Introduction

In recent years, sustainable development and increasing fuel demand necessitates the identification of possible energy sources [1]. In the world wide, many countries are paying great attention to the exploration of bioenergy which is regarded as a renewable and clean energy due to its renewable nature, carbon dioxide-neutral characteristics, and world-wide availability [2]. Particularly, a goal has been set by the Chinese government that 50 million tons of biomass pellets will be produced and used annually by 2020 [3].

In China, corn is one of the most important cereal crops, which is extensively planted, and the yield of corn has reached 215 Mt in 2014 according to China Statistical Yearbook of 2014 made by China's National Bureau of Statistics. As a kind of green renewable energy, cornstalk (CS) and corncob (CC) are the main by-products from the processing of corn. Generally, the CS resources can be retained on farmlands by corn harvesters, while the CC resources may be collected, transported and separated together with the corn grain, and serve as a raw material in making low-grade fuels in many parts of the world [4]. Therefore, the thermal conversion techniques used to convert biomass are various such as combustion, gasification, pyrolysis, hydrogen production, and so on [5,6]. These bioenergy conversion techniques can be used to produce high quality products. However, the use of the biomass as fuel also generates large amount of residual ash which may cause some serious environmental problems. As a result, the biomass ash is easy to melt and volatilize [7]. During the thermo-chemical conversion process, the residual inorganic materials also forms slag

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inside boiler and fly ash depositing on the tail heating surface, which retard heat transfer, deteriorate burning, cause high temperature corrosion and super-heater explosion [8–10].

With respect to other bioenergy conversion methods, gasification has received considerable attention for the conversion of biomass into synthesis gas, which mainly contains CO, H_2, CH_4, and other hydrocarbons [11]. Nowadays, there are more than six hundred biomass gasification stations running and producing normally in China, which can supply synthesis gas for more than two hundred thousand households. But during the biomass gasification process, the biomass ash with complexly chemical composition and high volatility can easily bond with tar and lead to the phenomena of slagging, fouling, and corrosion in the thermal conversion systems [8,12]. The characterization of different biomass ashes are quite different. So far, there exist many research works that have been done to study the characterization of biomass ash by experiment and simulation [6,9,10,12–18]. But there are only few studies on the characterization and utilization potential of corncob ash (CCA) derived from gasification in the world wide. Therefore, the further study on the properties and utilization potentials of CCA is very important, which will be helpful for improving slagging and promoting the effectively use of biomass resources.

Gasification and combustion are thermochemical conversion methods that are used to convert biomass to energy [18]. Since these ash residues derived from gasification process and combustion process are generated under different conditions, thusly, it can be sure that the physical and chemical properties of gasification ashes are typically different from the combustion ashes. The aim of this study is to obtain information about the basic properties, utilization potential, and agglomeration behavior of the corncob fly ashes from gasification process, and this is compared with inorganic ashes generated by combustion of the corncob feedstock at 600 and 815 °C, respectively. After comparing the results of physical and chemical properties between these two types of solid residues, their potential utilization applications were evaluated. In this study, the basic characteristics of CCA derived from different processes were investigated by using laser particle size analyzer (LPSA), X-ray fluorescence spectrometer (XRF), X-ray diffractometer (XRD), scanning electron microscopy and energy dispersive X-ray (SEM-EDX), thermogravimetric and differential thermal analyzer (TG-DTA). These basic characteristics mainly involve particle size distribution, chemical content, mineral phases, morphology, and thermal behavior. In addition, the effects of ashing temperature on the morphology, elemental composition, and agglomeration behavior of CCA were also determined.

2. Experimental section

2.1. Raw ash from corncob gasification

The gasification ash used in this study were collected from the cyclone dust collector of a corn cob sourced biomass gasification station, which located in the peripheral rural area of Shenyang, northeastern China. This gasification station can provide synthesis gas simultaneously for about 300 households. And it is equipped with a synthesis gas purification system consists of three basic components: cyclone dust collector, spray-dryer system and tar scrubber.

The ash samples were first pulverized by a ball mill due to the severe non-homogenity, then placed into a pan and oven dried at 105 ± 0.5 °C for 24 h. After the ash samples were dried and cooled, they were again grounded and homogenized, and finally sieved with a 0.154 mm sieve prior to analyses.

2.2. Preparation of the combustion ashes

There is no specific standards are available for preparation of biomass ash in China. Hence, in order to obtain the differences/similarities of performance properties and agglomeration behavior between CCA from gasification and that from combustion, the ashing temperatures of corncob were set at 815 and 600 °C according to the standards for coal ash preparation in China (GB/T212-2008) and ASTM standards in America (ASTM E1755-01).

The corncob used in the preparation of combustion ashes was also obtained from the peripheral rural area of Shenyang, China. Table 1 presents the proximate and ultimate analysis of the used corncob sources.

Prior to preparation of the combustion ashes, the corncob samples were dried under natural conditions, and grinded via a grinder. Then they were sieved with a 100 mesh sieve, and the pulverized corncob samples were put in a Muffle furnace (SX2-15-12, Dongtai Shuangyu Instruments Co, Ltd., Jiangsu, China) and kept for 2 h at temperatures of 815 and 600 °C, respectively. The storage interval of furnace was 1 °C and the atmosphere was air. The processing procedures for the combustion ashes were completely the same to those of gasification ashes, which were first pulverized, then dried and sieved with a 0.154 mm sieve.

2.3. Determination of the ash characterization

Chemical analysis of CCA was determined by X-ray fluorescence (ZSX100e. Rigaku Co., Japan). The mineral phases present were determined by X-ray diffraction using a Cu Kα radiation of 0.15406 nm (X'Pert PRO, PANalytical B.V., Netherlands). Major peaks were identified through comparison with standards of High Score Plus software package. Scanning electron microscopy (Ultra Plus, Carl Zeiss Co. Ltd., Germany) and energy dispersive X-ray (Genesis, Edax DX-4) were employed to obtain more information on the ash, such as ash morphology, possible agglomeration phenomena, and surface composition of ash powders. Prior to analysis, the ash samples were gold-coated for making them electrically conductive. Thermal and differential thermal analysis was finished by using a thermal balance (NETZCH-STA449 F3, Germany) to obtain the weight loss and phase transition. For each test about 5 mg samples were heated at the rate of 20 °C/min till a temperature of 1200 °C. The total unburnt carbon content of CCA was quantitatively determined by elementary analysis using a Vario MACRO Elemental Analyzer of Elementar, Germany.

3. Results and discussion

3.1. Particle size distribution

Fig. 1 shows the particle size distribution for the CCA powders from gasification through a 0.154 mm sieve. As seen from Fig. 1, there exist two graphs for the ash particle size, one is the particle size distribution graph, and the other is the cumulative frequency distribution graph. Fig. 2 shows the micrograms of the sized and ground CCA powders obtained at 600 and 815 °C, respectively. The main results of granularity analysis for all ash samples are summarized in Table 2.

As for the CCA powders from gasification, the mean diameter and the medium diameter of the sieved powders are 12.96 μm and 10.23 μm, respectively. The accumulated percentage for the ash powders within diameter of 30 μm occupies more than 90%. Specifically, with respect to 600 and 815 °C CCA derived from combustion process, the specific surface area of CCA from gasification in the as seized condition is much larger, which is roughly 1.46 m^2/cm^3, indicating that more volatiles are released from the solid substrates in the gasification process. Besides, the expansion

Table 1
Proximate and ultimate analysis of the corncob (on air dried basis).

Proximate analysis (wt.%)				Ultimate analysis (wt.%)				
Moisture	Ash	Volatile matter	Fixed carbon	C	H	O	N	S
0.87	2.24	79.25	17.64	47.26	5.79	43.23	0.56	0.05