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Research article

Effects of temperature and low-concentration oxygen on pine wood sawdust briquettes pyrolysis: Gas yields and biochar briquettes physical properties

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ABSTRACT

Biochar briquettes have advantages of higher energy volume density and durability, as well as the convenience for storage and transportation. In this paper, the effects of temperature and O_2 concentration on gas yields and biochar briquettes physical properties were investigated. The yields of H_2 and char decreased with the increase of temperature and O_2 concentration. An increase in the temperature and O_2 concentration led to an increase in CO_2 and CO yields. The CH_4 yield reached the highest value of 23.46 g/kg at 800 °C with 4% O_2. Higher temperature than 600 °C and O_2 concentration than 6% were not good for the volume density and durability rating but were beneficial for the porosity of biochar briquette. The BET surface area and total pore volume of O_2-char was higher than those of N_2-char produced at the same temperature. Considering comprehensive analysis of temperature requirements, char yield and physical properties, 500 °C and 6% O_2 were the optimal oxidative pyrolysis conditions.

1. Introduction

Biomass pyrolysis is a thermal chemical conversion technology which can transform a variety of recalcitrant feedstocks into liquid, solid, and gaseous fuels, meanwhile generating both heat and power [1]. In China, forestry wastes, such as pine wood, can be reused as a kind of easy-to-access and concentrated biomass resource. As a waste of underutilization, pine wood and its sawdust briquette has a great-potential in the production of value-added products via pyrolysis [2].

Oxidative pyrolysis is a fundamental thermal chemical conversion process and is regarded as an important technique in biomass utilization. Pinewood oxidative pyrolysis took place in three stages: drying, volatiles emission and char oxidation whereas only the first stage occurred under inert conditions [3]. Under oxygen concentrations, the releasing characteristics of CO, CO_2 and H_2 were significant affected by the oxygen concentration. The time for completely releasing the gas components was shorted with increasing temperature and oxygen concentration. At high oxygen concentration, the activation energy for forming CO and CO_2 increased while the activation energy of H_2 formation decreased [4]. The presence of oxygen had an appreciable effect at all heat flux levels, which is most prevalent at low heat fluxes [5]. Besides, the maximum heat evolved in oxidative environments is relatively constant and similar for all conditions tested. All the production of detected non-condensable gases, such as H_2, CH_4, CO_2, NH_3, NO and NO_2 were favored by oxidative conditions [6]. The condensable gases except H_2 are released over narrower temperature ranges with-oxygen concentration increased. It was confirmed that the thermal reactivity of biomass (especially the cellulose) was greatly enhanced due to the acceleration of mass loss by oxygen [7]. Thermal degradation and emission rates of carbon oxides proceed at lower temperatures for the particles with smaller size [8]. Oxygen had a strong influence on pyrolysis behaviour in a non-isothermal apparatus with a low heating rate [9]. Nevertheless, the particle size had a significant influence on conversion: transfer phenomena limit oxidative pyrolysis in the high heating rate non-isothermal apparatus. The same authors performed another study to investigate the impact of air flux and bed bulk density on the behavior of the oxidation zone in terms of wood consumption, and yields of char, gas and tars [10].

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However, few papers focus on the effect of temperature and low-concentration oxygen on biomass briquettes pyrolysis and its potential effects on the reaction. Biochar briquettes have advantages of higher energy volume density, higher unit heating value, better water-resistivity and durability than sawdust biochar, as well as the convenience for storage and transportation [2,13]. As a result, biochar briquettes have a significant potential to be applied in thermal power plants and metallurgical processes to replace the traditional fossil fuel. The objectives are to:(1) determine influence of oxygen concentration on the gas yields and biochar briquettes physical properties; (2) investigate the effects of temperature and low-concentration oxygen on biomass briquettes pyrolysis reaction; (3) propose a mechanism to illustrate the role of low oxygen during biomass briquettes pyrolysis under different temperatures.

2. Experimental

2.1. Raw material properties

The pinewood sawdust was acquired from a furniture factory in Kunming. Proximate analysis of pinewood sawdust was performed using Thermo-gravimetric Analyzer (TGA701), and ultimate analysis was performed according to ASTM D 5382. Heating value of the raw materials were determined by PARR 6200 automatic bomb calorimeter. Prior to analysis, the raw materials were milled and sieved in a size range of 0.15–0.18 mm. The sieved particles were put in a drying system at 105 °C for at least 24 h prior to use. Proximate and ultimate analyses and lower heating value of pinewood sawdust are listed in Table 1.

2.2. Briquetting process

2 ± 0.1 g raw powder materials were put into a cylindrical metal mold. It's well known that heat and pressure have a positive effect on solidness of briquette [14,15]. All the samples were pressed in a heating presser and kept at a working pressure of 15 MPa with a temperature of 100 °C for 1 min. The produced briquettes presented to be a cylindrical shape with 20 ± 0.02 mm in length and10 ± 0.01 mm in diameter. Thus the energy consumption of each sawdust briquette in briquetting process ($EC_{briquetting}$) was estimated for size reduction, compression and heating stages, which can be calculated by Eq. (1).

$$EC_{briquetting} = W_{size} + W_{press} + W_{heating} = Pt + \frac{\pi}{4}\int_0^{1.5}\int_0^{0.03} dpdx + C_p m\Delta t \quad (1)$$

With: W_{size} is the energy consumption for size reduction (kJ); W_{press} is the energy consumption for compression (kJ); $W_{heating}$ is the energy consumption for heating stage (kJ); P = the rated power of pulverizer (kw); t is the grinding time (s); C_p is specific heat of powder sawdust at constant pressure (kJ/kg°C); m is the mass of powder sawdust (g); Δt is temperature difference (°C).

Besides, the volume density (D_V) of powder sawdust and briquette were respectively 0.5095 g/cm^3 and 1.2738 g/cm^3. In addition, the lower heating value of powder sawdust and briquette are the same 17.77 MJ/kg. After densification, the obtained energy density of sawdust briquette can be calculated by Eq. (2).

Table 2
Parameter of energy consumption and obtained energy for the production of each sawdust briquette.

Energy consumption type	Unit (kJ)
W_{size}	0.027
W_{press}	0.035
$W_{heating}$	0.089
$ED_{obtained}$	21.323

$$ED_{obtained} = LHV \times (D_{V2}\text{-}D_{V1}) \times V_{briquette} \quad (2)$$

With: LHV = the lower heating value of powder sawdust and briquette (MJ/kg); D_{V2} = The volume density of sawdust briquette (g/cm^3); $D_{V1}$is the volume density of powder sawdust (g/cm^3); $V_{briquette}$ = the volume of sawdust briquette (cm^3).

The overall parameter of energy consumption and obtained energy for the production of each sawdust briquette is shown in Table 2.

It is obvious that $ED_{obtained}$ is higher than $EC_{briquetting}$, which shows that hot sawdust densification is feasible and worthwhile.

2.3. Pyrolysis procedure

The pyrolysis experiments were carried out in a fixed-bed reactor. Firstly, one pinewood sawdust briquette (2.0 ± 0.1 g) was placed in a quartz tube reactor (35 mm i.d., 220 mm length), and then high-purity nitrogen was flushed to evacuate the air in the system before pyrolysis. The flow rate of the pyrolysis gas medium (pure nitrogen or mixtures of oxygen and nitrogen) was set to 50 ml/min. The O_2 concentration (0, 2, 4, 6 and 8%) was adjusted by changing its rate via a mass flow-controller. Then the reactor was placed into a preheated furnace (400,500,600,700 and 800 °C), and maintained at the desired temperature for 30 min. The gas yields were calculated by weighting the sampling Tedlar bag and after the pyrolysis. After that, the final gas (CO_2, CO, H_2, CH_4) yield and composition were subsequently analyzed with a gas chromatography analyzer (Agilent 7890A GC). The cooling and drying systems were used to avoid water condensation inside the bag, which could distort the measurements. In concentration, the yield of the residual char was quantified by weighting the quartz tube before and after the pyrolysis. N_2 was continuously pumped into the furnace to decrease furnace temperature and maintain inert atmosphere until the biochar briquettes would not be oxidized. After the biochar briquettes were collected for 24 h, the height and diameter of biochar briquette was measured respectively by caliper gauge. To assure the reliability of the test results, each test was repeated three times, and the final results were presented as an average.

2.4. The pyrolysis products yields

The quantity of N_2 collected in the bag was known, and its molar fraction was given by the GC. So it was feasible to determine the total moles of gas in the bag and to calculate the molar quantity of the aforementioned gaseous species.

The yields of gases are given hereafter as mass yields on a air-dried basis (g gas/kg wood):

Table 1
Proximate and ultimate analyses and lower heating value of the pinewood sawdust.

Proximate analysis (wt%, ad)				Ultimate analysis(wt%, daf)					Lower heating value
Volatile	Ash	Fixed carbon	Moisture	C	H	O[a]	N	S	MJ/kg
79.72	0.51	16.11	3.66	49.11	5.55	44.91	0.0.41	0.02	17.77

Ad: Air-dried; daf: Dry ash-free.

[a] Content is obtained by difference.