Fuel Processing Technology 153 (2016) 43–49

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Thermal & chemical analyses of hydrothermally derived carbon materials from corn starch

Min Zhao [a], Bin Li [a,*], Jia-Xiao Cai [a], Chuan Liu [b], K.G. McAdam [b], Ke Zhang [a,c,**]

[a] Zhengzhou Tobacco Research Institute of CNTC, Zhengzhou 450001, China
[b] Group Research & Development, Regents Park Road, Southampton SO15 8TL, UK
[c] School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China

ARTICLE INFO

Article history:
Received 29 December 2015
Received in revised form 29 July 2016
Accepted 1 August 2016
Available online 6 August 2016

Keywords:
Hydrothermal carbonization
Thermogravimetric analysis
Kinetics
Microstructure
Pyrolysis

ABSTRACT

Hydrothermal and pyrolytic carbonization were used in this study to prepare a range of carbonaceous materials from corn starch powder. The objective of the study was to investigate the relationship between microstructures of the hydrothermally carbonized materials synthesized by a two-step carbonization process and their thermophysical and thermochemical properties. Differences in thermal behavior, as observed by thermogravimetric measurements conducted in air, were investigated by supplementary studies using elemental and proximate analysis, Fourier transform infrared spectrometry (FTIR), X-ray photoelectron spectroscopy (XPS) characterisation and weight loss kinetic modeling. The results indicated that the degree of the aromatization of obtained materials with higher carbon contents could be increased by subsequent annealing at higher temperatures. The resulting materials with different carbon skeletons displayed different kinetic behavior upon heating. Kinetic modeling of the thermogravimetric data revealed a low temperature and a high temperature combustion region with different kinetics parameters, thus demonstrating the potential of hydrothermal carbonization (HTC) as a synthesis strategy for fine-tuned functional high-purity combustion fuel preparation.

1. Introduction

Sustainable and green energy development is a global challenge. Charcoal can play an important role for sustainable energy consumption if it can be made economically through non-fossil fuel based routes. Conventional charcoal production usually involves thermochemical conversion of biomass (e.g., wood, coconut shell, or other agricultural byproducts) or coal [1,2]. Charcoals with more specific surface properties have been made via petrochemical route [3] or secondary treatments of charcoal with surface modification [4]. Research on nano-structured carbon-based materials biomedical and electronic applications has also attracted significant interests. In general, however, research is still needed to shift both the source materials and the energy used to more sustainable bases for economically viable charcoal materials. For this reason, different biomass have been used as source materials for carbonaceous fuels [5] and also for bioenergy [6,7].

In the last decade or so, hydrothermal carbonization (HTC) of biomass has attracted increasing interest in the field of carbon materials and biofuels [8]. Bergius first described the hydrothermal transformation of cellulose into coal-like materials in 1913. Early work mainly focused on the preparation of biofuels [9]. The full potential of hydrothermally carbonized materials has only been discussed in recent years through the work of Titirici and co-workers [10,11], in several fields such as catalysis, CO_2 sequestration, agriculture and renewable energy products.

Typical energy contents of HTC materials have been measured to be between 25 and 35 $MJ \cdot kg^{-1}$, which is about 40% higher than those of biomass precursors [12]. The HTC materials are expected to exhibit favourable behaviors with respect to combustion, gasification, and other thermal conversion processes. There have also been studies on combustion or gasification of carbon materials [13,14]. The most important issue in combustion or thermo-synthesis of carbon materials, such as fullerenes, nanotubes, graphite, and diamond, is the control of compositional, morphological and chemical nature of different carbon sources reacting with an oxidant agent [15–16]. However, as far as we are aware, there has been no systematic work on combustion characteristics of HTC materials.

The objective of this study was to conduct a feasibility of using corn starch as a model precursor, due to the defined mechanism under HTC conditions, to evaluate the link between various carbonized products as a combustion fuel. The combustion characteristics of different HTC intermediates from corn starch, its post-carbonization forms, and the carbon derived from pyrolysed corn starch were investigated to understand the relationship between the microstructural properties and combustion characteristics. A range of experimental techniques were

---

* Corresponding author.
** Correspondence to: K. Zhang, Zhengzhou Tobacco Research Institute of CNTC, Zhengzhou 450001, China.
E-mail addresses: ztrilibin@163.com (B. Li), hfzhangke@126.com (K. Zhang).

http://dx.doi.org/10.1016/j.fuproc.2016.08.002

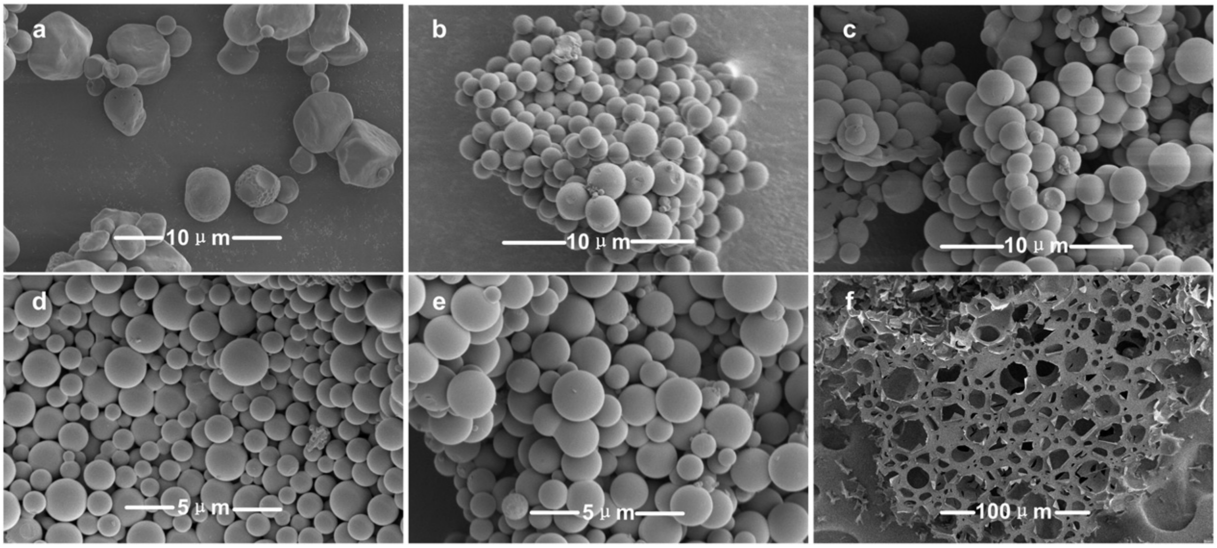

Fig. 1. SEM images of (a) corn starch, (b) HTC-S, (c) HTC-S-350, (d) HTC-S-550, (e) HTC-S-750, (f) Py-S-550.

employed such as scanning electron microscopy (SEM), N_2-adsorption/desorption, Fourier-transform infrared spectroscopy (FTIR), elemental and proximate analysis of the materials, X-ray photoelectron spectroscopy (XPS) and non-isothermal thermogravimetrics analysis. In addition, kinetic analysis based on the Coats-Redfern model was performed on the HTC materials combustion processes [17,18].

2. Materials and methods

2.1. Materials

Corn starch powder was purchased from Aladdin Reagent Co. Ltd. (Shanghai, China) and was used as received. Deionized water used was from A. S. Watsons Group Ltd. (Shanghai, China). All other reagents used in the synthesis were of analytical grade.

2.2. Preparation of carbon materials

HTC material, its post-carbonization forms, and pyrolytic carbon were prepared and studied following the methods described below. For preparing the HTC materials, 70 mL deionized water was mixed with 6.3 g corn starch power and the solution was placed into a 100 mL Teflon lined stainless steel autoclave at room temperature. The autoclave was sealed and heated in an oven for 12 h at 180 °C. The HTC material obtained was separated from the remaining aqueous solution by centrifugation at 7000 rpm for 20 min and then washed 5 times with deionized water and ethanol. Finally, the derived material was dried in a vacuum oven at 80 °C for 12 h. The sample material thus prepared is labeled as “HTC-S”.

Pyrolysis was performed in a horizontal tube furnace with a $20\ \text{mL} \cdot \text{min}^{-1}$ nitrogen flow rate at 350 °C, 550 °C, and 750 °C, respectively. The heating rate was $10\ \text{K} \cdot \text{min}^{-1}$. The carbon source materials were the starch and its HTC form (HTC-S). All the samples were held at the final temperature for 4 h before being cooled to room temperature by the nitrogen flow. They were then homogenized by grinding with a mortar and pestle. The post-carbonization HTC-S is denoted as HTC-S-X and the pyrolysed starch as Py-S-X; in both cases, “X” is denoted as the carbonization temperature (350, 550, or 750 °C). For example, Py-S-550 is a pyrolysis-derived carbon material heated at 550 °C under nitrogen atmosphere.

2.3. Characterization

The morphology of the prepared samples was characterized using JEOL-6010LA scanning electron microscopy (SEM). Before imaging, sample powder was loaded onto Kapton carbon tapes and sputtered with Au. Images were acquired by setting an SEM working distance of 10 mm and accelerating voltage of 1.5 kV. In addition, the surface area, total pore volume, and average pore diameter of the synthesized samples were calculated by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The measurement was carried out at 77 K using the adsorption of nitrogen gas (Micromeritics, Model ASAP2020). Fourier transformed infrared (FTIR) spectroscopy measurements were carried out at room temperature in ambient atmosphere using a Nicolet 6700 FTIR spectrometer with the KBr pellet technique. FTIR spectra were recorded in the range of $4500–400\ \text{cm}^{-1}$. The spectral outputs were recorded in the transmittance mode as a function of wave-number and 124 scans were recorded with the resolution of $4\ \text{cm}^{-1}$. The X-ray photoelectron spectra (XPS) were recorded with an ESCALAB 250 (Thermo Electron). The X-ray excitation was provided by a monochromatic Al Kα (1486.6 eV) source. Data quantification was achieved by the advantage program.

Elemental chemical analysis of the samples were carried out in a CHONS Elemental Analyzer (Vario El Cube, Elementar, Germany) to determine C and H contents in a stream of pure O_2. The content of oxygen was calculated by subtracting the relative C and H fractions. Proximate analysis is based on thermogravimetry [19], containing moisture (M, wt.%), volatile matter (VM, wt.%), fixed carbon (FC, wt.%) and ash (A, wt.%) contents.

Table 1
Surface area and pore characteristics of corn starch, HTC-S, its post-carbonization forms, and pyrolytic carbon material.

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
Starch	0.8	–	–
HTC-S	3	0.02	23
HTC-S-350	26	0.05	6
HTC-S-550	496	0.27	2
HTC-S-750	512	0.27	2
Py-S-550	437	0.24	2