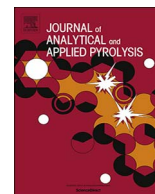




Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Short communication

Direct synthesis of hollow carbon nanofibers on bio-char during microwave pyrolysis of pine nut shell

Jian Zhang^a, Arash Tahmasebi^a, Joy Esohe Omoriyekomwan^a, Jianglong Yu^{a,b,*}^a Key Laboratory of Advanced Coal and Coking Technology of Liaoning Province, School of Chemical Engineering, University of Science and Technology Liaoning, Anshan, 114051, China^b Chemical Engineering, University of Newcastle, Callaghan, NSW 2308, Australia

ARTICLE INFO

Keywords:

Hollow carbon nanofibers
Bio-char
Microwave pyrolysis
Carbon structure

ABSTRACT

Hollow carbon nanofibers (HCNFs) were formed on the bio-char surface during microwave pyrolysis of pine nut shell in the temperatures range of 400–700 °C without the use of any additional catalyst, except activated carbon added as a microwave absorber. Scanning electron microscopy (SEM) analysis showed that HCNFs were only formed on microwave pyrolysis chars and not fixed-bed chars, suggesting that microwave irradiation had a major influence on their formation. High resolution transmission electron microscope (HRTEM) results showed that the synthesized HCNFs at 500 °C and 600 °C had a diameter of about 400 nm and length of 1400–5000 nm. HCNFs had multi-walled structure with a d-spacing of about 0.35 nm. Unlike fixed-bed bio-chars, the X-ray diffraction (XRD) analysis of the microwave bio-chars showed typical graphite peak at around $2\theta = 26.3^\circ$ with the strongest peak observed in 600 °C bio-char. Raman spectroscopy analysis revealed that the highest degree of carbon order of HCNFs was achieved at 600 °C, which agreed well with XRD analysis results. Detailed analysis of the volatiles evolved during microwave pyrolysis suggested that hydrocarbons in bio-oil such as benzene and alkenes and CO, CO₂, methane, and ethane in bio-gas acted as the carbon source during formation of HCNFs.

1. Introduction

Carbon nanofibers (CNFs) were first discovered on the surface of catalyst products during pyrolysis of hydrocarbon and the disproportionation reaction of carbon monoxide in the late 19th century. However, detailed research was not carried out until carbon nanotubes were discovered by Iijima in 1991 [1]. The diameter of CNFs (50–200 nm) are between that of carbon nanotubes (< 50 nm) and the vapor-grown carbon fibers (300–1000 nm). CNFs have cylindrical structures with stacked platelet, ribbon, or herringbone graphene sheets stacking arrangement [2]. CNFs exhibit high thermal and electrical conductivity as well as high mechanical strength and find wide applications in energy storage and conversion devices, catalyst support, high strength composites, sensors, direct methanol fuel cells (DMFCs), solar panels, aerospace industry, and nanoelectronic devices [3–8]. CNFs have been synthesized using a number of methods such as electrospinning, laser ablation, arc discharge, chemical vapor deposition (CVD), spray method, etc. [9]. However, these methods require the use of a transition metal or alloys as catalyst for the decomposition of an external carbon source and operate at high temperatures and the complexity of operation, low energy efficiency, and the use of external

catalyst and carbon source make them difficult to scale up. Therefore, alternative technologies need to be developed for efficient synthesis of CNFs from renewable energy sources [10].

As a renewable and low-cost source of carbon, biomass has great potential for sustainable production of carbon materials. Chen et al. [11] synthesized CNFs using activated carbon produced from agricultural waste by chemical vapor deposition. Shi et al. [12] used microwave-induced processing for synthesis of multi-walled CNTs from gumwood. They postulated that the generation of active sites and self-assembly of graphitized carbon under microwave was likely the mechanism of CNTs formation.

Further research is required for understanding the mechanism of formation and growth of CNFs using biomass as source material under microwave irradiation. In this study, the synthesis of hollow carbon nanofibers (HCNFs) from pine nut shell biomass and without any catalyst addition and at relatively low temperature (500–600 °C) via microwave-induced pyrolysis was investigated. The optimum reaction temperatures for the synthesis of carbon nanofibers were determined systematically. The structure of HCNFs formed on bio-char during microwave pyrolysis was studied in detail by using various analytical methods and the formation and growth mechanism of HCNFs was proposed.

* Corresponding author at: Key Laboratory of Advanced Coal and Coking Technology of Liaoning Province, School of Chemical Engineering, University of Science and Technology Liaoning, Anshan 114051, China and Chemical Engineering, University of Newcastle, Callaghan, NSW 2308, Australia.

E-mail address: jianglongyu@163.com (J. Yu).

<https://doi.org/10.1016/j.jaap.2018.01.016>

Received 13 October 2017; Received in revised form 2 January 2018; Accepted 14 January 2018

0165-2370/ © 2018 Elsevier B.V. All rights reserved.

2. Materials and methods

2.1. Materials

Pine nut shell (PNS) from North China was used as the biomass feedstock for microwave pyrolysis experiments. The PNS sample was crushed and sieved to a particle size of 65–200 μm and dried subsequently in a vacuum oven at 105 $^{\circ}\text{C}$ for 10 h to remove moisture. The mineral matter composition of PNS biomass was measured using X-Ray Fluorescence Spectrometer (XRF, shimadzu1800, Japan). Since biomass is not a good microwave receptor, a commercially available biomass-based activated carbon (AC, Chengde activated carbon Co., Ltd., China) was used as microwave receptor in order to reach pyrolysis temperatures under microwave irradiation. Similar to microwave pyrolysis, PNS samples were mixed with activated carbon during fixed-bed pyrolysis in order to isolate the effect of heating mode on formation and growth of CNTs. The particle size of AC was higher than 200 μm to facilitate the separation of bio-char and AC by sieving after pyrolysis. The elemental composition of PNS biomass and activated carbon samples was measured using Euro Vector Euro EA elemental analyzer. The proximate and ultimate analyses of the PNS biomass and the activated carbon are presented in Table 1.

2.2. Fixed-bed pyrolysis experiments

The detailed procedure of fixed-bed pyrolysis experiments can be found in our previous study [13]. Briefly, the pyrolysis experiments were carried out using a tubular quartz reactor with an internal diameter of 2.0 cm heated in an electric furnace. A nitrogen flow of 400 ml/min was used during the pyrolysis experiments. The pyrolysis runs were carried out at final temperatures in the range of 400–700 $^{\circ}\text{C}$ for 20 min. About 8.0 g of biomass was mixed with AC prior to heating at a mass ratio of 8:2. The fixed-bed pyrolysis runs were repeated at least twice to ensure the results were reproducible. The temperature profile of the samples was measured using a thermocouple. The heating rate of the samples under fixed-bed condition was in the range of 108–152 $^{\circ}\text{C}/\text{min}$, increasing at higher target temperatures.

2.3. Microwave-induced pyrolysis experiments

The schematic diagram of the microwave pyrolysis experimental setup can be found elsewhere [14]. Microwave pyrolysis experiments were carried out in a self-designed quartz reactor (with an internal

Table 1
Proximate and ultimate analyses of pine nut shell, activated carbon, and EDS analysis of HCNFs.

Composition	Pine nut shell	Activated carbon	HCNFs (EDS analysis)
Elemental analysis (wt.%, daf)			
C	50.16	90.57	98.67
H	5.81	0.66	–
N	0.28	0.32	–
S	ND	0.18	–
O ^a	43.41	4.57	1.1
K	0.37	0.52	0.14
Si	0.21	–	0.09
Ca	0.12	–	–
Mg	0.015	–	–
Al	0.008	–	–
Proximate analysis (wt.%, ad)			
Moisture content	2.12	0	–
Volatile matter	74.53	6.88	–
Fixed carbon	22.63	89.44	–
Ash content	0.94	3.68	–

ad: air dried; daf: dry ash free.

^a Calculated by difference.

diameter of 5 cm), placed in a microwave oven (Tangshan Microwave Thermal Instrument Co. Ltd., China) with maximum power output of 2000 W and frequency of 2.45 GHz. About 8.0 g of biomass was physically mixed with AC at a mass ratio of AC to biomass of 8:2 using a glass rod. A high purity nitrogen gas (99.999%) was used as carrier gas with a flow rate of 400 ml/min in pyrolysis experiments. The temperature of sample bed was measured using a thermocouple inserted into the sample mixture and was recorded at 2 s intervals. In order to investigate how the thermocouple itself interacts with microwave, a blank experiment was carried out using thermocouple in the quartz reactor. The results showed that the temperature of thermocouple increased from 30 $^{\circ}\text{C}$ to 55 $^{\circ}\text{C}$ after 5 min microwave irradiation with a very slowly heating rate and remained relatively stable thereafter. These results indicated that microwave was not absorbed significantly by the thermocouple and the increase in sample bed temperature was the result of microwave adsorption by the sample mixture. Pyrolysis runs were carried out for 20 min at final temperatures of 400, 500, 600, and 700 $^{\circ}\text{C}$. The final pyrolysis temperatures were reached within three min under current experimental conditions. The heating rate of the samples ranged between 126 $^{\circ}\text{C}/\text{min}$ and 226 $^{\circ}\text{C}/\text{min}$, increasing with the target temperatures. Upon reaching the desired temperature, the microwave oven equipped with automatic temperature control system maintained the desired temperature by adjusting the output power level. Bio-chars were separated from activated carbon by sieving based on the difference in their particle size. The microwave pyrolysis experiments were repeated twice, so that the reproducibility of the results could be confirmed.

2.4. Characterization of bio-char and HCNFs

The morphology and microstructure of bio-chars were characterized using scanning electron microscope (SEM, ZEISS Sigma HD) and high-resolution transmission electron microscope (HRTEM; JEM-2100F, JEOL, Japan, 200 kV) with energy dispersive spectroscopy (EDX) auxiliary. The composition of HCNFs was characterized using EDX analysis. The crystallinity of the HCNFs was studied using an X-ray diffractometer (XRD, Rigaku Ultima IV) with a Cu X-ray tube ($\lambda = 1.5406 \text{ \AA}$) and Lynx Eye detector. The 2θ was ranged from 10 $^{\circ}$ to 60 $^{\circ}$ with a step scanning rate of 2 $^{\circ}/\text{min}$. Raman spectroscopy (Horiba Jobin Yvon Xplora plus) equipped with a 532 nm laser diode was used to characterize the carbon structure and order of HCNFs. Thermogravimetric analysis (TGA) (NETZSCH STA 449F3) was also used to determine the yield of HCNFs. Bio-chars derived from microwave pyrolysis were burned in air at 450 $^{\circ}\text{C}$ for 2 h and the yield of HCNFs were calculated by subtracting the ash content in biomass from the residual weight of bio-char combustion.

2.5. Characterization of pyrolytic volatiles

The composition of pyrolysis volatiles including bio-oil and bio-gas were determined in order to identify the possible carbon sources for the formation of HCNFs. The pyrolysis volatiles were passed through three consecutive condensers containing dichloromethane (a total of 900 ml) and placed in ice water to capture the bio-oil. Bio-oil was separated from dichloromethane by distillation and analyzed using a gas chromatography-mass spectrometer (GC-MS, Thermo Scientific ISQ) equipped with a capillary column coated with TR-5MS (cross-link 5% Phenyl (equiv.), Polysilphenylene-siloxane, 30 m length, 0.25 mm inner diameter) and a quadrupole analyzer operating in electron impact (70 eV) mode. The oven was heated at 10 $^{\circ}\text{C}/\text{min}$ from 40 to 100 $^{\circ}\text{C}$, and then at a heating rate of 15 $^{\circ}\text{C}/\text{min}$ from 100 $^{\circ}\text{C}$ to 280 $^{\circ}\text{C}$, and held at 280 $^{\circ}\text{C}$ for 15 min. Chemical compounds in bio-oil were identified by comparing their mass spectra to spectral data in the instrument database. The pyrolytic bio-gas was analyzed using a gas chromatograph (GC; Thermo Scientific ISQ). GC was equipped with a thermal conductivity detector (TCD) with a molecular sieve column capable of

Download English Version:

<https://daneshyari.com/en/article/7606411>

Download Persian Version:

<https://daneshyari.com/article/7606411>

[Daneshyari.com](https://daneshyari.com)