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Preparation of Fe-cored carbon nanomaterials from mountain pine beetle-killed pine wood ☆

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ABSTRACT

The mountain pine beetle-killed lodgepole pine (*Pinus contorta*) wood treated with iron (III) nitrate solution was used for the preparation of Fe-cored carbon nanomaterials (Fe-CNs) under various carbonization temperatures. The carbonization yield of Fe-treated sample (5% as Fe) was always 1–3% higher (after ash compensation) than that of the non-treated samples heated at the same condition. The lowest carbonization temperature required to produce Fe-CNs was 700 °C. The carbon shell was composed of 30–40 well-aligned layers of graphitic carbon nanostructure. The iron captured by graphitic layers was assumed to be iron carbides and/or α-Fe and γ-Fe. This study indicates that at least 700 °C of carbonization temperature is needed for the production of Fe-CNs and the mountain pine beetle-killed pine wood can be a carbon source for the production of Fe-CNs.

1. Introduction

Biomass materials, such as wood, have been processed with a thermal chemical method under different combinations of temperatures and processing times. Our previous study results showed that different sizes, shapes, structures, and chemical compositions of amorphous, porous, and crystalline carbon-based nanomaterials (CBNs) can be prepared from pine wood chars which are by-products from the fast pyrolysis process using an Auger reactor [1–3]. In recent years iron nanoparticles have become important materials for a wide range of applications in the field of biosensing, drug delivery, data storage, magnetic resonance imaging and catalyst [4,5]. However, maintaining iron nanoparticles in zero-valent state is not easy because they can be rapidly and completely oxidized in air. Encapsulation of iron nanoparticles by graphitic carbon is one of the solutions to protect oxidation from oxygen in the air.

On the other hand, in the north-eastern part of the US and Canada, the infestation of mountain pine beetle (*Dendroctonus pondersae*) is widely spreading and can result in extensive tree mortality. One of the recommended methods to reduce this infestation is to thin infested trees. However, these smaller diameter thinning trees have limited value for structural use [6].

The goal of this study was to investigate the feasibility of preparation of value-added Fe-cored carbon nanomaterials (Fe-CNs) from mountain pine beetle-killed lodgepole pine (*Pinus contorta*) wood with the specific objective of studying the temperature effect on formation of Fe-CNs from it.

2. Experimental

Materials: A plastic bag of the beetle-killed pine wood chips (approximately 0.375 in. by 0.070 in., moisture content: 4.38%) was received from USDA-Forest Products Laboratory for this experiment. To prepare samples for iron treatment, a portion of wood chips was first ground by a Wiley Mill, followed by passing the wood meal through a 1 mm mesh screen. Iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) purchased from Sigma-Aldrich (98% purity) was used as an iron source.

Carbonization without Fe-catalyst: The carbonization of wood chips without Fe-catalyst was carried out in a stainless steel cylinder (4 in. by 0.51 in.) inserted into a split-hinge tube electric furnace (Lindberg/Blue M 1200) equipped with a temperature controller (Lindberg/Blue UTC 150). Eight temperature levels from 300 to 1000 °C with an increment of 100 °C were evaluated under atmospheric pressure with an argon gas at a flow rate of 100 ml/min. For each temperature run, 1.4 g of wood chip was put into the cylinder.

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The carbonization process started with the argon gas flowing through the cylinder system for 15 min to remove oxygen from the system, followed by raising the temperature to the evaluated temperature level at a ramping rate of 20 °C/min. After holding the final temperature for 1 h, the cylinder was allowed to cool down to room temperature, and carbonized materials were removed from it and weighed. The carbonization yield of each temperature run was calculated by

$$X\% = (A/B) \times 100 \quad (1)$$

where A is the weight of carbonized materials after carbonization, and B is the weight of oven-dried wood chip before carbonization.

Carbonization with Fe-catalyst: The ground wood meal of 410 g (air dried, moisture content: 5.08%) was mixed with $Fe(NO_3)_3$ solution [150 g of $Fe(NO_3)_3 \cdot 9H_2O$/2 L of de-ionized water]. The content of Fe in wood meals was 5% of the wood meal weight. The slurry of the mixture was placed in an aluminum tray for 24 h at ambient temperature and stirred occasionally. The mixture was dried in a convection oven at 110 °C for 2 days, and then packed in a Ziploc bag. The moisture content of the Fe-treated pine wood (Fe-PW) was 6.74%. 2 g (based on oven-dried weight) of Fe-PW was heat-treated under the same thermal process condition as samples without Fe-catalyst. The carbonization yield of Fe-PW was estimated by

$$Y\% = (C/D) \times 100 \quad (2)$$

where C is the weight of carbonized materials after carbonization with ash content deducted from the total weight, and D is the weight of oven-dried wood meal before carbonization with ash content deducted.

Characterization: Powder X-ray diffraction (XRD) was performed with a Rigaku SmartLab X-ray diffractometer (Rigaku) using Cu Ka radiation ($\lambda = 1.5418$ nm). Field emission scanning electron microscopy (FE-SEM) images were obtained by a JSM-6500F (JEOL). For high-resolution transmission electron microscopy (HRTEM), samples were further ground in ethanol by an agate mortar to reduce their size and then a drop of this suspension was dripped onto a 200 mesh copper grid with a holey support film. HRTEM analysis was performed on a JEM 2100F (JEOL) equipped with an EDAX (Ametek).

3. Results and discussions

Carbonization yields of Fe-treated wood meals and non-Fe-treated wood chips from experiments performed in this study are presented in Table 1. The carbonization yield of pine wood chips without Fe catalyst (N-PW) calculated using Eq. (1) gradually decreased as the carbonization temperature increased from 300 to 600 °C and then maintained at a constant level of 18–19% as the temperature further increased from 600 to 1000 °C. This result is similar to the one reported by Mun et al. [7], and also in the yield range from 15% to 25% commonly reported for wood carbonized under an anaerobic condition. When Fe-PW was subjected to the same carbonization temperature as N-PW, its yield at each evaluated temperature estimated using Eq. (2) with the weight of ash content deducted from the total weight was always about 1–3% higher than that of N-PW. During measurement of the ash content of Fe-PW samples, it was observed at the ash content of Fe-PW samples was 7.78%, which was higher than 5%, the content of Fe added to pine wood meal before carbonization. This ash content weight increase indicated that iron nitrate in the wood meal was oxidized during the experimental procedure of determination of ash content, i.e., iron oxides were produced because of oxygen.

There was no carbonization yield reported in Table 1 for Fe-PW samples heat-treated in the temperature range from 400 to 600 °C because at this temperature range the carbonized samples were spontaneously ignited and burnt when the cylinder unit was opened. It was reported that naked metallic nanoparticles are chemically highly active, pyrophoric and are readily oxidized upon the contact with air to produce their oxides [8]. Thus, this indicates that the iron nitrate used in this experiment as a catalyst changed to Fe nanoparticles at the carbonization temperature range from 400 to 600 °C, but they were not completely covered by carbon shells and eventually spontaneously ignited when they were exposed to air. This phenomenon indicates that the Fe-cored carbon shell structure starts its shell formation at the temperature range of 400–600 °C.

Table 1
Carbonization results of Fe-treated and non-treated pine wood.

Carbonization temperature (°C)	Carbonization yield (%)		
	Without Fe	With Fe	
		Before ash subtraction	After ash subtraction
300	29.65	41.16	33.38
400	23.01	ND	ND
500	20.20	ND	ND
600	18.72	ND	ND
700	19.18	28.77	20.99
800	18.22	28.50	20.72
900	18.58	28.78	21.00
1000	17.75	28.90	21.12

ND: Not determined because the sample was spontaneously ignited and burnt when the carbonization was finished and the cylinder was opened.
Note: The yield value in Table represented the average of 2–4 replicates run for each temperature level. Their coefficients of variation ranged from 0.10% to 3.79%.

Fig. 1 illustrates XRD patterns of N-PW and Fe-PW carbonized under the temperatures from 600 to 1000 °C, respectively. Graphite diffraction peaks usually appear at $2\theta = 26°(002)$, 42.9°(100), and 43.7°(101) [1]. In the case of N-PW samples, these peaks appeared to be broader at 600 °C, and became narrower as the temperature increased. The amorphous carbon region with the diffraction intensity less than 15°gradually decreased as temperature increased. This indicates that the degree of pine wood graphitization is significantly affected by heating temperature. In the case of Fe-PW, graphite diffraction peaks ($2\theta = 26°(002)$) clearly appeared on all carbonization temperature levels from 700 to 1000 °C. In addition, many Fe-related peaks were also observed. Some of these peaks were assigned as iron oxides (Fe_2O_3, Fe_3O_4) [9], but strong and sharp diffraction peaks appearing at 43–46° were assumed to be iron carbides (FeC_3, Fe_3C, FeC_2, Fe_7C_3, etc.) or α-Fe ($2\theta = 43.4°$) and γ-Fe ($2\theta = 44.6°$) [10–13]. It was reported that a pure iron carbide such as Fe_3C in high yield can be prepared by reducing iron oxide in the presence of carbon monoxide at temperatures from 500 to 550 °C [10]. Arabczyk et al. [11] also reported the preparation of nanocrystalline iron carbide by reduction of iron with methane under atmospheric pressure at 580 °C. Methane, carbon monoxide, and hydrogen are usually generated as pyrolysis products during wood carbonization at temperatures higher than 500 °C. Therefore, it is no surprise that the iron carbides can be formed under our carbonization conditions. The formation of carbides was confirmed with further analysis of our experimental data.

Fig. 2 shows the low and high magnification FE-SEM images of Fe-PW samples carbonized at 1000 °C. The surfaces were covered with nanoparticles with sizes less than 100 nm in their diameters, while N-PW samples had a smooth surface and no nanoparticles observed. In addition, there were many nanomaterials packed in the broken-fiber-like materials. These FE-SEM results can also imply that many carbon nanostructures could be formed in the

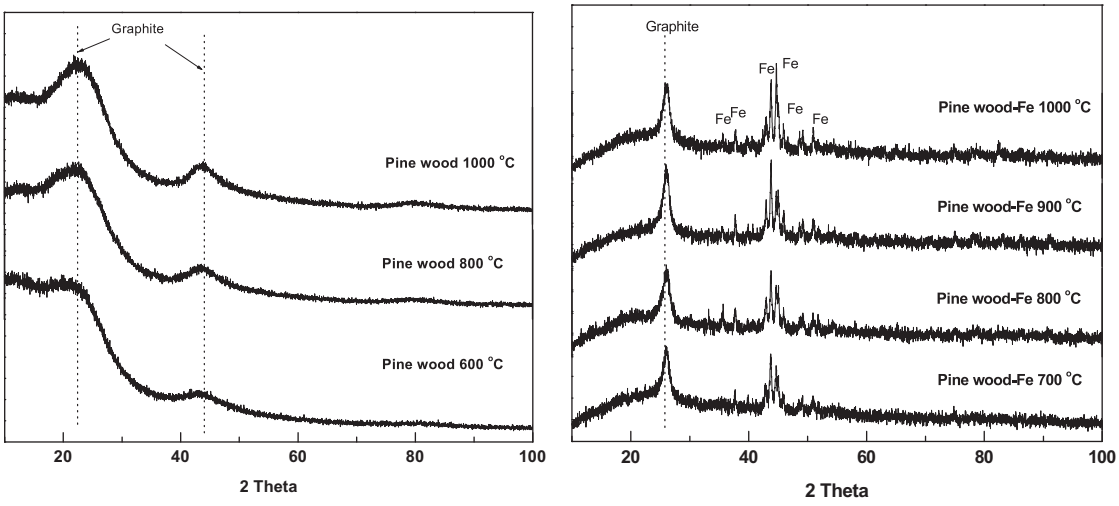

Fig. 1. Power X-ray diffraction (XRD) patterns of carbonized N-PW (left) and Fe-PW (right) at different carbonization temperatures.

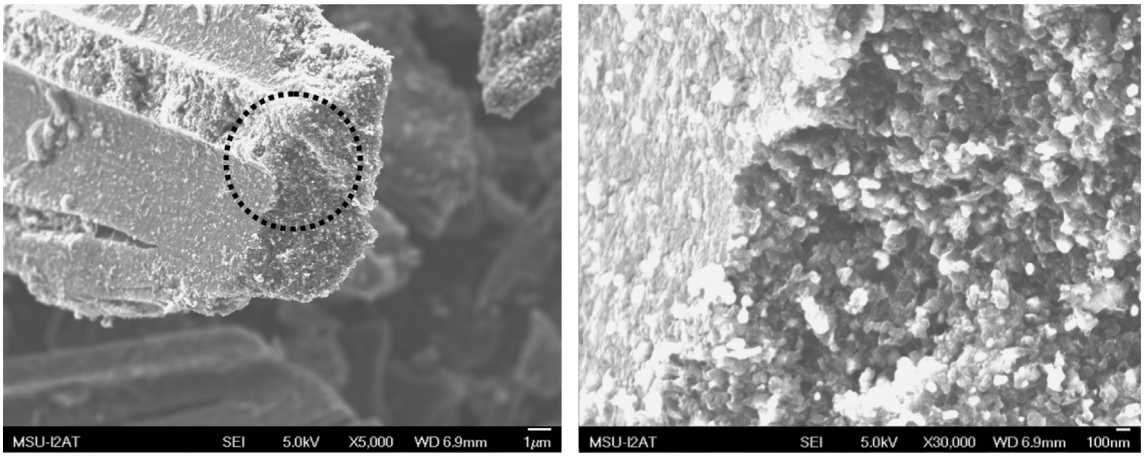

Fig. 2. FE-SEM images of carbonized Fe-PW samples prepared at carbonization temperature of 1000 °C. Right image is the magnification of circled parts of left image, which show that the size of observed nanomaterials is less than 100 nm.

carbonized Fe-PW samples. The HRTEM analyses were performed to further confirm the formation of carbon nanostructures in Fe-PW samples. Fig. 3 shows the HRTEM images of Fe-PW samples carbonized at 700 °C, with well-aligned and multilayered (30–40 graphitic layers) graphitic carbon structures. These graphitic carbon nanostructures are tangled together, and the appearance is like multi-walled carbon nanotubes, but they are not carbon nanotubes. The average interlayer spacing of these graphitic layers calculated was 0.338 nm, which is almost the same as the graphite (002) plane. Approximately 20-nm iron nanoparticles captured by multi-walled carbon shells were also observed. These iron nanoparticles are similar to the particles produced by Mun et al. [1] by thermally treating wood char with Fe nanoparticles (25 nm in average diameter) as the catalyst, but having more graphitic layers than the particles reported by Mun et al. [1] which had 15–17 graphitic layers. Therefore, it is concluded that the carbonization with about 5% Fe-treated pine wood can lead to the production of Fe-cored carbon nanostructures with a simple thermal treatment under relatively lower temperature in comparison with a wood charcoal production process.

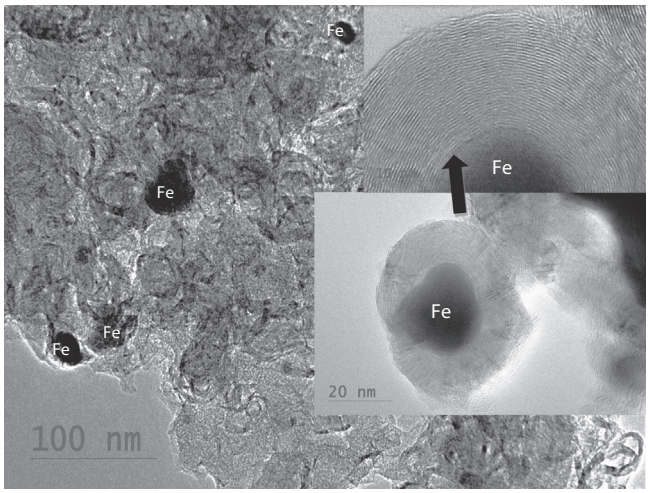

Fig. 3. HRTEM images of carbonized Fe-PW samples at 700 °C.

4. Conclusions

The mountain pine beetle-killed pine wood was used for the preparation of Fe-CNs. The carbonized samples prepared from N-PW showed similar carbonization patterns and yields as reported in other pine wood carbonizations. The carbonization yield of Fe-PW samples (treated with 5%) was always 1–3% higher (after ash compensation) than that of the N-PW samples heated at the same condition. The lowest carbonization temperature required to produce carbon shell captured Fe nanoparticles was found to be 700 °C. The carbon shells

were composed of well-aligned, and 30–40 layered graphitic carbon nanostructures. The iron captured by graphitic layers was assumed to be iron carbides and/or α-Fe and γ-Fe. In conclusion, this study showed that the mountain pine beetle-killed pine wood can be used as a good carbon source for the production of Fe-CNs. In addition, we found a suitable carbonization temperature for producing these nanomaterials.

Acknowledgments

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