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Synthesis and Characterization of Carbon Nanospheres Obtained by Hydrothermal Carbonization of Wood-derived and Other Saccharides

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Carbon nanospheres were synthesized by hydrothermal carbonization (HTC) of four different carbon sources: xylose, glucose, sucrose, and pine wood derived saccharides. The obtained carbon nanospheres were characterized for particle morphology and size, and surface functional groups. Morphological and structural differences among these saccharides derived HTC carbons were clearly observed. Scanning electron microscopy images of carbon nanospheres from HTC of xylose showed uniform spherical particles with diameters around 80 nm, while carbon nanospheres obtained from glucose, sucrose, and pine-derived saccharides had particle size in the range of 100-150 nm, 300-400 nm, and 50-100 nm, respectively. Carbon dioxide and carbon monoxide were primary gaseous phase products during the HTC process. In addition, methane, propane, hydrogen, and benzene were detected in the gas phase.

Keywords: Hydrothermal Carbonization (HTC); Carbon Nanospheres; Carbohydrates; Pine Wood-derived Saccharides; Gas Phase Composition; Mechanism of HTC

1. Introduction

Carbonaceous materials have been widely used in diverse industries due to their superior properties such as good electrical conductivity, high surface area and porosity, and their specific surface chemistry. Carbonaceous materials are produced from carbon-containing compounds by thermal, chemical or hydrothermal processes in gas, liquid, or solid phases [1]. The physical and chemical properties as well as the structure of formed carbons are affected by both reaction conditions and the feedstock [2]. Various feedstocks such as cyclohexane and acetylene have been used to produce nanoscale carbons. However, these raw sources were not sustainable or renewable and these processes were usually expensive. Therefore, the objective of this work is to develop a simple process to produce nanoscale carbon particles with renewable materials such as pine wood-derived saccharides.

In the current effort, the hydrothermal carbonization (HTC) method was examined, and saccharides derived from pinewood were used as the feedstock. A HTC

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process with moderate temperatures and self-generated pressures over an aqueous solution of a variety of feedstocks in a dilute acid for hours is a promising process to produce nanostructured carbon materials from woody biomass [3]. The carbon content in wood varies from 47 to 53% due to differences in lignin and extractives contents [4]. Chemical components of loblolly pine woods are 42-46% glucose in cellulose, 1-5% glucose, 10-11% mannose, 7% xylose, 1-2% arabinose, and 1.5-2.5% galactose in hemicelluose, and 27-30% lignin, which makes a total carbon contribution of 66-69% [5]. Almost 30 to 50% of carbon in wood could be converted to the solid char via thermochemical processes.

For this study, highly functionalized carbonaceous materials were synthesized from four different carbon sources (xylose, glucose, sucrose, and carbohydrates derived from pine wood) by using a moderate temperature HTC process. The carbon nanospheres from xylose had a perfect spherical shape with the highest yield among all feedstocks used. The gas phase composition of the reaction effluent was analyzed, and carbonaceous materials were characterized using the scanning electron microscopy (SEM), the transmission electron microscopy (TEM), and the temperature-programmed desorption (TPD). The possible mechanism of the HTC of saccharides was proposed.

2. Materials and Methods

2.1 Materials

All compounds such as xylose, glucose, sucrose, and sulfuric acid (95%) were purchased from Sigma-Aldrich. The wood chips used were raw southern yellow pinewood chips.

2.2 Preparing Pine Wood Derived Saccharides

Saccharides were obtained via sulfuric acid hydrolysis of the southern pine wood chips (<10 mm in length) [6]. The pine wood chips were dried to a moisture content of ~10% in an onsite dryer, and treated with 72% H_2SO_4 (15 g chips in 150 mL acid solution) at 30ºC for 1 h. The mixture of acid treated pine chips was diluted by adding 4,200 mL of water and hydrolyzed at 121ºC for 1 h. Then, the hydrolysate solution was filtered through the crucibles with a filtering disc to separate the filtrate and residues. The filtrate containing saccharides was used to prepare carbon nanoparticles.

An Agilent 1100 high-performance liquid chromatography (HPLC) (Santa Clara, CA) was used to analyze saccharide concentrations in the filtrate. The HPLC consisted of a G1311A liquid chromatograph pump, G1379A online degas unit, G1313A automatic injector with a 20 µl loop, and G1315B diode array detector. The column was Agilent Hi-Plex Ca, 7.7 × 300 mm, 8 µm (p/n PL1170-6810), the mobile phase was de-ionized (DI) H_2O with a flow rate of 0.6 mL/min, and oven temperature was 85ºC. The structural carbohydrates in pine wood were determined according to the standard analytical procedure [6]. The filtrate (*i.e.* the hydrolysate produced from the pine wood) contained 33.3% (w/v) glucose, 4.8% (w/v) xylose, 1.4% (w/v) arabinose, 2.9% (w/v) galactose, and 15.4% (w/v) mannose.

2.3 Synthesis of Carbon Nanospheres by Hydrothermal Carbonization

2.3.1 Preparation of Carbon Nanospheres from Glucose, Sucrose and Xylose

The hydrothermal carbonization of glucose was carried out using following procedures: Sixty gram of glucose was dissolved in 1000 mL DI water and stirred for 0.5 h to form a clear solution. Concentrated sulfuric acid (~95%) was added dropwisely to adjust the pH value of the solution to between 4~5. Then, the solution was transferred to a stainless steel 1 gallon Parr reactor (Moline, IL), and heated and maintained at 180°C with continuous stirring for 12 h. After the hydrothermal carbonization process was completed, the Parr reactor was then cooled to room temperature with continuous stirring. The gas phase (about 5~10 psig) in the Parr reactor was first released and analyzed with a Dycor-Dycor Dymaxion Residual Gas Analyzer (RGA) (AMETEK Process Instruments, Pittsburgh, PA). The obtained black slurry mixture was separated by centrifugation, washed with DI water and ethanol, and dried at 80°C overnight. The procedures for preparing carbon nanospheres from sucrose and xylose were the same as that of glucose.

2.3.2 Preparation of Carbon Nanospheres from Pine-derived Sugars

A 250 mL pine-wood-derived sugar solution, which contained ~30 g saccharides, was used as the starting material. The pH value of the solution was adjusted to 3. The sugar solution was stirred for 0.5 h in a beaker, and then transferred into a Parr reactor. The solution was heated and maintained at 210°C for 12 h. The black solid products were collected and washed with DI water and ethanol to remove soluble ions and sugar residues. The final product was oven-dried at 110°C overnight.

2.4 Characterization of Carbon Materials

The sample morphology was investigated with a Scanning Electron Microscope (SEM) (JEOL JSM-6500F, Peabody, MA). The system was operated with accelerating voltage of 5 kV. All samples were coated with gold. The sample particle sizes were examined with a JEOL JEM-100CX II transmission electron microscope (TEM, Peabody, MA). TEM was operated at accelerating voltage of 100 kV. All samples were sonicated in ethanol solution for 20 min before transferred on copper grid. Thermogravimetric analysis (TGA, Shimadzu TGA-50，Japan) was performed to determine the weight loss during calcination. For each sample, the temperature was ramped at 10 °C/min to 1000°C under atmosphere. Temperature-programmed desorption (TPD) experiments involved heating the carbon nanospheres at 2 °C/min in a helium gas to induce thermal desorption of adsorbed species on the surface. Volatile species were analyzed using an on-line Agilent 7890 GC during the TPD process. A 5 g sample were carried out in a fixed-bed 1/2-inch tubular stainless-steel reactor under N_2 atmosphere (99.999 % purity) at a flow rate of 20 ml/min.

3. Results and Discussion

3.1 Hydrothermal Carbonization of Saccharides

Experimental conditions of the HTC of saccharides including samples, reaction temperature, and reaction time are summarized in Table 1. The results showed that the highest and lowest carbon nanospheres yields were obtained from xylose and sucrose, respectively. The difference in yields may be due to different carbonization tendencies of these saccharides. Xylose began to decompose and carbonize at about 140 °C, while the decomposition temperature for glucose and sucrose was between 160-170 °C. Among all starting materials studied, xylose was the best raw material to get the highest yield of the carbon nanospheres.

Table 1 Synthesis conditions and product yields for carbon nanospheres obtained from the HTC of saccharides

Sample	HTC temperature (°C)	Reaction time (h)	Yield of nano-materials (g product/100 g saccharides)	Size (nm)
Xylose	180	12	80.2	~80
Glucose	180	12	68.5	100-150
Sucrose	180	12	54.7	300-400
Pine wood derived saccharides	210	12	60.3	50-100

3.2 Gaseous Products from Hydrothermal Carbonization

The composition of gases resulted from the HTC of glucose was analyzed with an on-line RGA (Figure 1). The RGA response showed that significant amounts of CO and CO_2 were released from the glucose. The results were consistent to Xue *et al.* [7], who have studied the pyrolysis of saccharides under different conditions and found that H_2O, CO, and CO_2 were released from the samples. The detection of benzene in the gas phase meant that aromatic species were important intermediates during the HTC process.

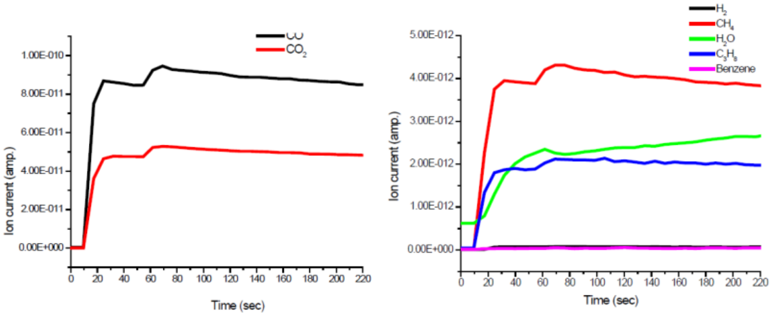

Figure 1 RGA of glucose after the HTC at 180°C.

The gaseous products were further analyzed using an Agilent 7890 GC, and the relative amount of 37.0 % H_2, 10.6 % CO, 45.3 % CO_2, 0.05 % C_2H_6, 0.001 % CH_4, 0.01 % C_3H_8, and 3.8 % N_2 were found in the gas phase. Trace amount of ethylene (less than 0.001 %) was also identified. The results of other saccharides were similar to that of glucose.

3.3 Characterization of Carbon Nanospheres

3.3.1 Scanning Electron Microscopy (SEM) Study

SEM images of carbon nanospheres produced by HTC are shown in Figure 2a-2d. Carbon nanospheres obtained from xylose (Figure 2a) had a higher degree of uniformity in shape and monodisperion compared to those by HTC of other saccharides, while carbon nanospheres derived from glucose and sucrose presented irregular shapes. The carbonaceous products from pine-derived saccharides exhibited a regular morphology (Figure 2d).

Under similar operational conditions, the diameter of nanospheres changed as a function of the type of saccharides used. Thus, the mean diameter followed the tendency: xylose (~80 nm) < glucose (120-150 nm) < sucrose (300-400 nm). This variation may be related to intermediate products decomposed from the different saccharides during the hydrothermal treatment process. The HTC of pentose like xylose proceeds via a furfural route, while hexose HTC occurs via a 5-hydroxymethylfurfural (HMF) route. Disaccharide like sucrose needs to be hydrolyzed into two mono-saccharides in the first step [3].

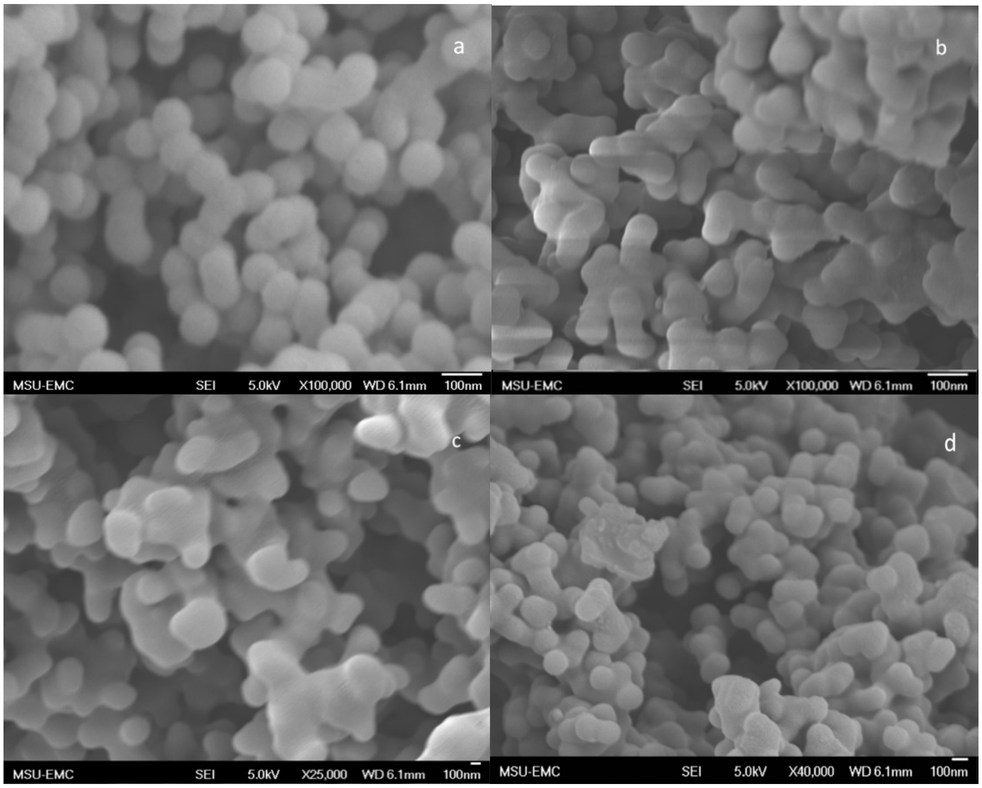

Figure 2 SEM images of carbon nanospheres by the HTC process at 180°C or 210°C. (a) xylose, (b) glucose, (c) sucrose, and (d) pine wood derived sugar solution

3.3.2 Transmission Electron Microscopy (TEM) Study

Figure 3 shows TEM images of carbon nanospheres from saccharides. The products made from xylose exhibited the diameter of approximately 80 nm (Fig. 3a), while glucose HTC products exhibit a tendency to form large agglomerates (Fig. 3b). The particle size from sucrose (400 nm) (Fig. 3c) is larger than that of xylose or glucose (120 to 150 nm). This is attributed to the longer C-C chains in sucrose. Similar to SEM images, TEM images (Figure 3d) show the presence of regularly shaped nanoscale carbons with diameters of 50-100 nm from pine derived sugar solution.

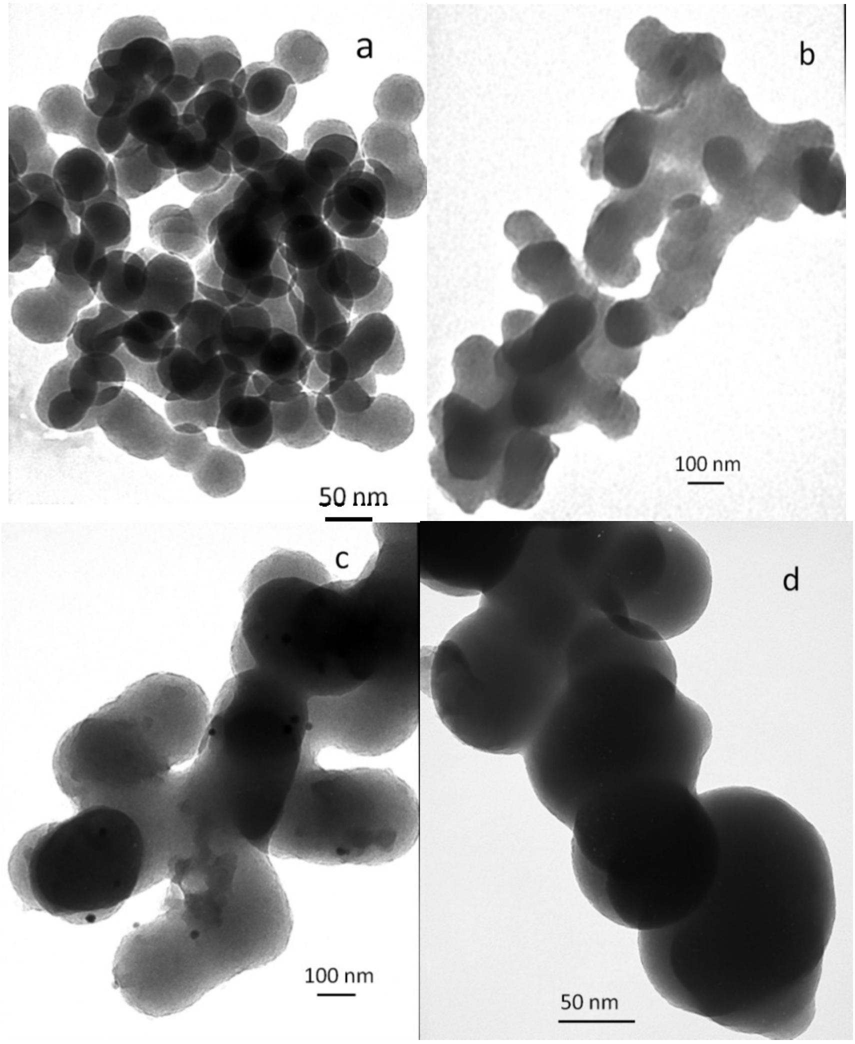

Figure 3 TEM images of carbon nanospheres by the HTC process at 180°C or 210°C. (a) xylose, (b) glucose, (c) sucrose, and (d) pine wood derived sugar solution

3.3.3 Temperature-Programmed Desorption (TPD)

TPD experiments coupled with an on-line GC were conducted to study the thermal desorption. The main decomposition by releasing gaseous compounds from carbon particles starting at 270°C was indicative of a restructuring of carbon motifs. The loss of volatile species such as H_2, CH_4, CO, C_2H_6, C_3H_8, and CO_2 was described by TPD spectra in Figure 4.

Between 400-500 °C, the strongest band intensities corresponded to the loss of CO_2 and CO, which decomposed from oxygenated functional groups. Surface complexes yielding CO_2 groups decomposed at two different temperatures, corresponding to two types of functional groups. Carboxylic acids ($-COOH \rightarrow CO_2$) were responsible for the low-temperature peak (100-400 °C), and the high-temperature CO_2 evolution was attributed to carboxylic anhydrides and lactones (450-700 °C). The CO-yielding groups were represented by three distinct groups of peaks, and the corresponding peak temperatures of CO desorption centered at 400°C for the anhydride and lactone groups. The CO peak centered at 500°C was assigned to the ether decomposition and the CO peak above 550°C was contributed to the phenols and quinine [8]. Subsequently at 500°C, the methane peak originated from decomposition of the methylene bridges, which acted as cross-linkers within the HTC carbon framework [9].

Hydrogen on the carbon surface served as chemisorbed water or as surface functionalities (*e.g.*, carboxylic acids, phenolic groups), or was bonded directly to carbon atoms as a part of aromatic or aliphatic structures. The C-H bond is very stable and will not break until 800 °C without catalyst. Heat treatment in an inert atmosphere eliminated part of the hydrogen via surface reduction. The carbonaceous surface contained a lot of oxygen-containing aromatic heterocyclic structures, which decomposed with the formation of carbon monoxide, methane, and other low hydrocarbons. As a consequence of the observed thermal decomposition processes, the structure of HTC carbons underwent a rearrangement process due to ring opening and aromatization.

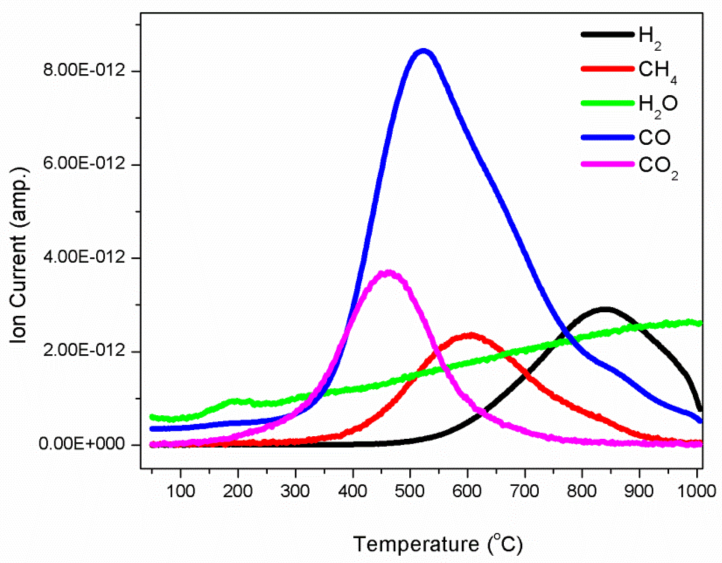

Figure 4 TPD curves for the temperature-programmed calcination of the carbon nanospheres from pine wood derived saccharides

3.3.4 Thermal Gravimetric Analysis (TGA)

Thermoanalytic techniques were used to study the thermal behavior of carbon nanospheres. The TG and DTG curves for the carbon nanospheres from pine-derived saccharides between room temperature and 700°C in N_2 atmosphere are shown in Figure 5. A continuous weight loss with increasing temperature was observed, which denoted breaking of chemical linkages and removal of volatile products from the sample. Three possible steps of weight loss could be observed in Figure 5. The initial weight loss may correspond to the loss of physically adsorbed water and occurred between ambient temperature and 130°C with a peak temperature of 70°C. It was followed by a plateau region for the rate of weight loss from 130°C to 200°C. The strong weight loss observed at around 200°C to 700°C corresponded to the decomposition of all the functional groups in the carbonaceous materials. These results indicated that oxygen functional groups started releasing in this temperature zone, leading to the initialization of aromatization. The most weight loss of carbon nanospheres was in the temperature zone from 350°C to 700°C. This mass loss step mainly attributed to the decomposition of the rest of the carboxylic anhydrides and lactones, part of phenols, quinine, and ether, which were released as volatile products such as CO_2, CO, CH_4, H_2O, and H_2.

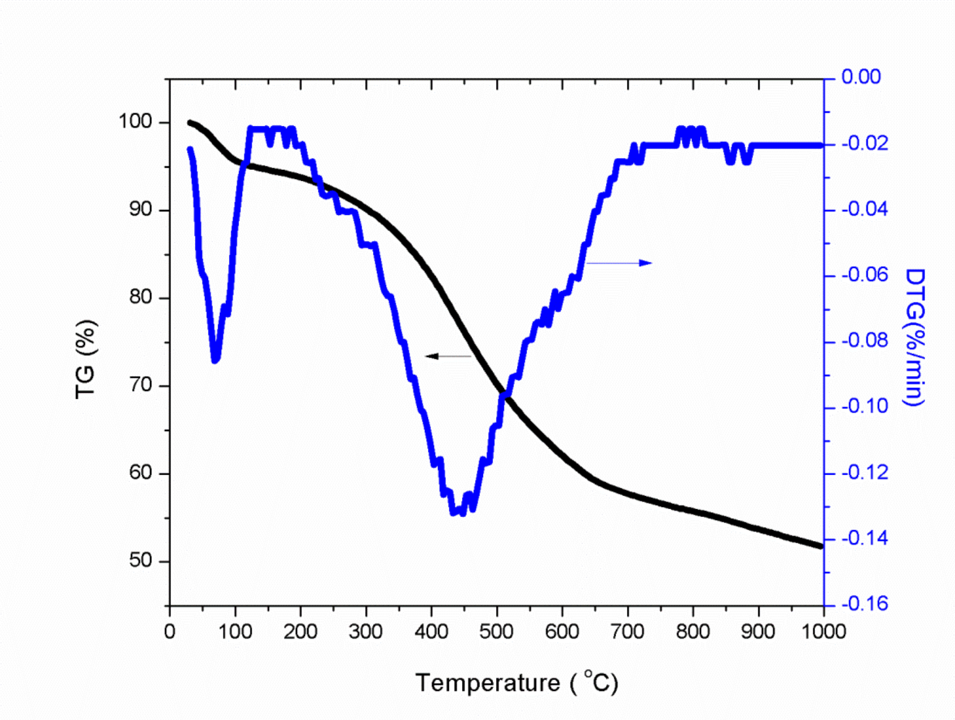

Figure 5 TG and DTG curves of the carbon nanospheres from pine wood derived saccharides

3.4 Possible Mechanism for Formation of Carbon Nanospheres

Based on the TPD spectra and gas phase composition presented upon completion of the HTC reaction, a possible mechanism of this process was proposed. The mechanism comprised two steps. In the first step, when an aqueous sugar solution was hydrothermally treated at 180°C, the sugar molecules (like glucose) hydrolyzed. In the second step, reactions consisted of both polymerization and condensation processes leading to the formation of soluble polymers [10]. Polymerization and condensation reactions may be induced by intermolecular dehydration or aldol condensation [8]. At the same time, the aromatization of polymers took place. The C=O group appeared due to the dehydration of water from the hydroxyl groups in the monomers [11, 12]. Aromatic clusters may be produced by the condensation of the aromatized molecules generated in the decomposition/dehydration of the oligosaccharides or monosaccharides [8]. All RGA results have demonstrated the presence of benzene in the gas phase. When the concentration of aromatic clusters in the aqueous solution reached the critical supersaturation point, the formation of carbon nucleation took place [8, 11]. The formed nuclei of carbon grew by diffusion of the chemical species present in the solution towards the surface [11]. These species were linked to the surface of the spheres via the reactive surface functional groups (hydroxyl, carbonyl, carboxylic, etc.) presented in the particles, which was proved by the experimental TPD spectra. Stable surface functional groups such as ether or quinone were formed. Once the growth process stopped, carbon nanospheres, whose surface contained a high concentration of reactive functional groups, were obtained. The gas phase composition and the TPD spectra of the carbon products were proved almost identical for all the saccharides investigated, indicating the similar mechanism for these saccharides.

4. CONCLUSIONS

This paper presented a systemic study on HTC of model saccharides (xylose, glucose, and sucrose) and carbohydrates derived from pine wood, producing carbon nanospheres with size between 50-400 nm. The carbon nanospheres from xylose had a perfect spherical shape with the highest yield among all feedstocks used. The mixture of saccharides from acid hydrolysis of pine wood can be used as carbon sources to synthesize 50-100 nm carbon nanospheres. The TPD proved that aromatization processes took place during the hydrothermal carbonization, and the carbon nanospheres contained a large number of oxygen functional groups. The shell contained hydrophilic oxygen functional groups (carboxylic, hydroxyl, etc.), while the core had hydrophobic aromatic nucleus with oxygen forming stable groups (ether, quinone, pyrone, etc.). During the thermal decomposition of derived carbon nanospheres, CO_2 and CO first decomposed from oxygenated functional groups, and then CH_4 and H_2 were released. Carbon nanospheres with surface oxygen groups and a controllable size possessed potentials for their further applications in hydrothermal carbon hybrid materials.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

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