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Original Article

Synthesis of carbon nanostructures by the pyrolysis of wood sawdust in a tubular reactor

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ABSTRACT

Carbon nanostructures were produced by wood sawdust pyrolysis. The results obtained revealed that the thermodynamic simulations (FactSage) were successful to predict the best reaction conditions for the synthesis of carbon, and potentially carbon fibers and nanotubes production. Graphite formation was indicated by XRD study, and by thermal analysis which presented the carbon oxidation range. The morphology of the samples (SEM/TEM analysis) showed carbon nanotubes/nanofibers varying in size and thickness, with defects and flaws. The tubular reactor was considered to be an economic and environmental correct way to nanomaterials growing, with the simultaneous generation of hydrogen and lower pollutant gas emissions.

1. Introduction

Several studies have shown interesting results in the use of wood waste to generate products with higher market valuation. There are examples in the field of building materials, composite materials, fertilizers and composting, absorbent medium, biofuels, among others [1–5].

Wood sawdust contains cellulose and this material can be used to produce carbonaceous materials in the form of carbon micro and nanostructures. According to the reaction conditions, it is possible to produce carbon fibers, carbon particles, nanoparticles, nanofibers and nanotubes in various configurations. Graphitic carbon nanostructures with coil morphology were produced by the hydrothermal treatment of cellulose via a dissolution–precipitation mechanism at 900 °C [6]. Lignocellulosic biomass from coconut coir was used to produce hollow carbon nanostructures by hydrothermal carbonization followed by pyrolysis in mild temperature conditions [7], and also the influence of clay mineral particles was analyzed [8].

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Hollow carbon nanostructures have also been synthesized before from cellulose by a three step processing: charring, high-temperature pyrolysis (CO_2 laser, ~2200 °C), and acid digestion [9].

Carbon structures have high thermal conductivity, chemical stability, high mechanical strength, electronic and magnetic properties, among others, and found application in many areas [10]. Currently, there is a great demand for nano-sized carbon materials, both for the study in applied research, as well as for industrial use. However, the developed processes often generate significant quantities of pollutants, especially in the form of gaseous emissions. Moreover, the production cost of nanomaterials is relatively high. Carbon nanotubes can be prepared by arc evaporation, laser ablation, pyrolysis and deposition, and electrochemical methods [11].

According to Mubarak [10]: "The production of carbons nanotubes (CNTs) using chemical vapor deposition (CVD) is the most promising method for possible industrial scale-up due to the its relative simplicity of operation, process control, energy efficiency, raw material used, capability to scale up as large unit operation, high yield and purity."

The study proposed in this paper shows that the reactor developed has a great potential to produce carbon nanostructures (nanotubes/nanofibers) at a very attractive cost [12]. This reactor uses waste wood as a carbon source and performs the burning (pyrolysis) with low emission of greenhouse gases, unlike other sources of carbon nanostructures. Moreover, the process does not use synthetic gases whose production is not always environmentally friendly, also reducing potential security risks in transport, handling and use. Besides the production of carbon structures, the pyrolysis of wood sawdust generates heat, and in appropriate conditions can generate hydrogen, which can be considered a clean fuel. Therefore, the process also presents significant environmental appeal.

2. Experimental

Wood sawdust was chosen because it is abundant, and due to the huge amount of waste generated in the wood industrial processes, particularly in the furniture production. Besides that, the wood structure with the presence of functional groups linked to carbon chain has natural potential for nanocarbon production. The method used for the experiments was the chemical decomposition of the wood sawdust. This material was mixed with the reducing agent (commercial zinc), calcite (bed material) and the catalyst (ferrocene or Fe/Mo/MgO) arranged in the column reactor, and then heated until 750 °C for 3 h without blowing air. These conditions were optimized according to the thermodynamic simulation performed with the FactSage software. It was used for each batch test: 10 g of sawdust; 2 g of ferrocene; 2 g of zinc, 5 g of calcite, and 0.6 g of clay.

2.1. Tubular reactor

It was designed and built a tubular reactor (Fig. 1) of stainless steel with 0.4 m long, internal diameter of 0.09 m, and two perforated plates in the upper and lower ends of the column. A mixture of wood sawdust, limestone and commercial zinc,

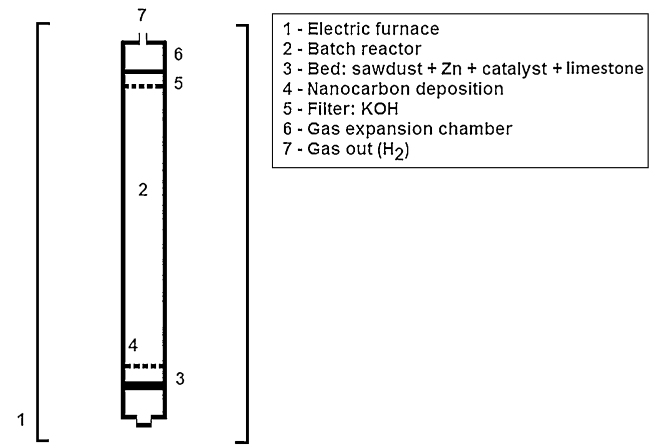

Fig. 1 – Scheme of the tubular reactor designed for nanocarbon synthesis.

which is used as a reducing agent in the system CO_2/C, is set on the bottom part of the column. At the top part, there is potassium hydroxide which helps to avoid releasing the emission of CO_2 and CO, retaining them in the form of salt (potassium carbonate). Thus, carbon nanotubes (CNTs) grow and occupy the lower portion of the column, where the catalysts are placed.

At the bottom of the column, there is an entrance for synthetic gases (e.g. argon, hydrogen or nitrogen as carrier gases to form an inert atmosphere) in the system (not used in the present study). The process is suitable for the employment of various atmospheres for the study of different kinds of carbon structures. Alternatively, the process can be modified to use the gas outlet at the top of the column. Thus, the gas phase and the particulate matter originating from the pyrolysis can be channeled out of the reactor, separated from the pyrolysis wastes, and after cool down, on a support or other reactor modulus, the synthesis of carbon nanotubes can be produced. This process can be summarized as wood pyrolysis and carbon vapor deposition on bed material and reactor walls.

Therefore, it can be noted that the process described above has potential for mass production of CNTs as shown in chemical vapor deposition processes with steam in a fluidized bed reactor [13,14].

2.2. Materials characterization

The samples were characterized using a scanning electron microscopy (JEOL JSM 6500F), transmission electron microscopy JEOL (JEM-2010), thermogravimetric analysis (TA 2050; heating rate of 10 °C/min, and flow synthetic air of 10 ml/min), X-ray diffraction analysis (Philips X'Pert), and Raman spectroscopy (Horiba Jobin-Yvon T64000; incident laser energy of 532 nm). The carbon nanotubes and fibers were not separated from catalyst residues and support, so impurities appear in the analysis, particularly in XRD and TGA. However, in SEM, TEM and Raman analyses it is possible to select the desired area of investigation to show details of carbon fibers and CNTs. The synthesized material was not subjected to any process of purification that would endear the product and therefore out of scope of the proposal. Therefore,