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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 nanosized 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, 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.

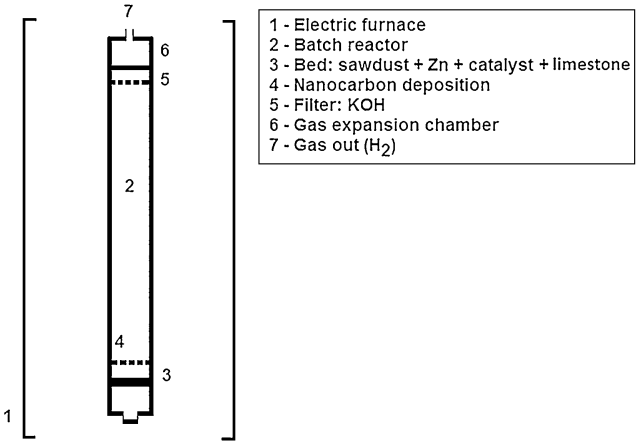

Fig. 1 – Scheme of the tubular reactor designed for nanocarbon synthesis.

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,

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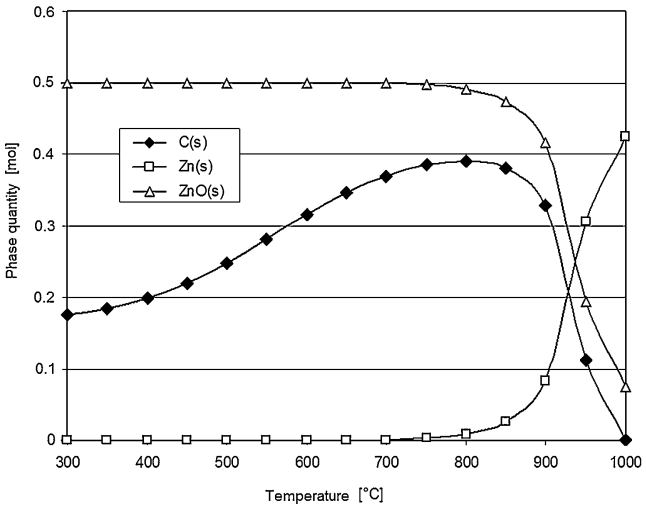

Fig. 2 – Thermodynamic simulation of temperature (°C) and relative concentrations (mol) for solid phases of C, Zn, and ZnO.

depending on the application, it may be necessary to perform a specific purification, as suggested by Ramesh [15].

3. Results and discussion

3.1. *Thermodynamic simulation of carbon and hydrogen synthesis*

Figs. 2 and 3 show the reaction conditions for the synthesis of carbon and gas generation during the process of burning the mixtures of wood sawdust and commercial zinc. The results were obtained using the software FactSage 6.4.

It can be seen in Fig. 1 that carbon is formed in high quantity in the temperature range of 700–800 °C. As a consequence of that, this temperature interval can be used to the tests in the tubular reactor.

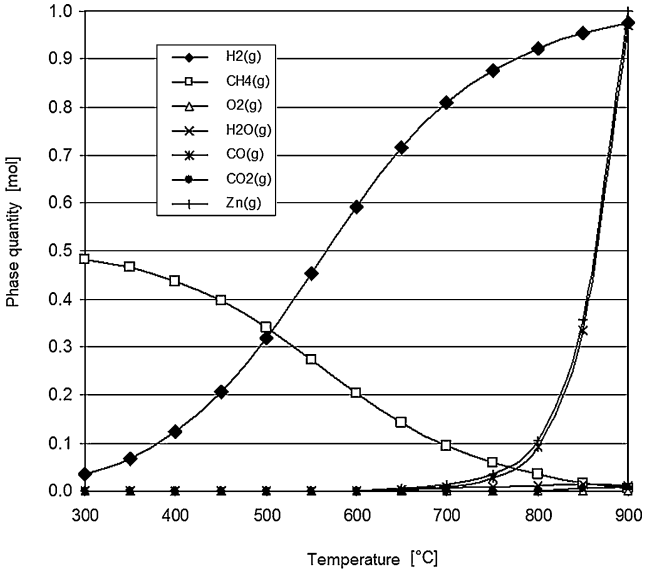

Fig. 3 – Thermodynamic simulation of temperature (°C) and relative concentrations of gases (mol) for H_2, CH_4, O_2, H_2O, CO, CO_2, and Zn.

Fig. 3 shows gas evolution during the pyrolysis of wood sawdust with zinc obtained in the thermodynamic simulation.

Fig. 3 shows that the decomposition of methane gas (CH_4) into hydrogen initiates at 300 °C and reaches its peak at ~800 °C, also with the release of hydrogen (and carbon formation). The overall reaction (1) according to thermodynamics at 750 °C is:

$$CH_4 \rightarrow C + 2H_2 \quad (1)$$

The oxidation of methane can proceed according to reaction (2)

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2 \quad (2)$$

At the same time, the zinc which is mixed with the wood sawdust contributes to the reduction of CO_2 and CO in carbon, keeping their concentrations low until ~750 °C, according to reactions (3) and (4):

$$CO_2 + 2Zn \rightarrow 2ZnO + C \quad (3)$$

$$CO + Zn \rightarrow ZnO + C \quad (4)$$

3.2. *Characterization of the synthesized material*

The batch tests were performed at 750 °C for the maximum synthesis of carbon and the simultaneous generation of hydrogen, according to the previous study of thermodynamic simulations. After burning all samples, the reactor bed and walls were completely covered by carbon deposition. The obtained material was characterized by TGA, XRD, SEM, TEM and Raman spectroscopy.

3.2.1. *Characterization of the catalyst support, bed material and carbon material*

The catalyst residues/support, bed material and carbon phase were initially characterized by XRD and TGA analyses.

The diffractogram in Fig. 4 shows the presence of graphite, but just a small peak, although its intensity is representative. It is also evident the mineral phases of the catalyst and bed material such as hematite, magnetite, zincite (reducing agent), calcite, and lime. This phase is formed due to partial decomposition of calcite, whose initial temperature of calcination and weight loss is ~700 °C [16]. Calcination of limestone is a highly endothermic reaction $\Delta H = +182.1\,kJ\,mol^{-1}$ [17], and this prevents temperature increasing locally.

The materials of the bed that were used to produce CNTs were chosen due to their compatibility to applications with construction concrete as a reinforced material, as can be seen in Fig. 4. The study of the development of 'new concrete' will be showed in other article. It is expected that CNTs/CFs perform as crack stoppers, improving fracture toughness of the concrete. However, there is no need to purification for using in concretes, according to the products showed in Fig. 4, e.g. lime, hematite, and illite. In addition, CNTs/CFs show non-wetting behavior in concrete formulation, what may not happen using

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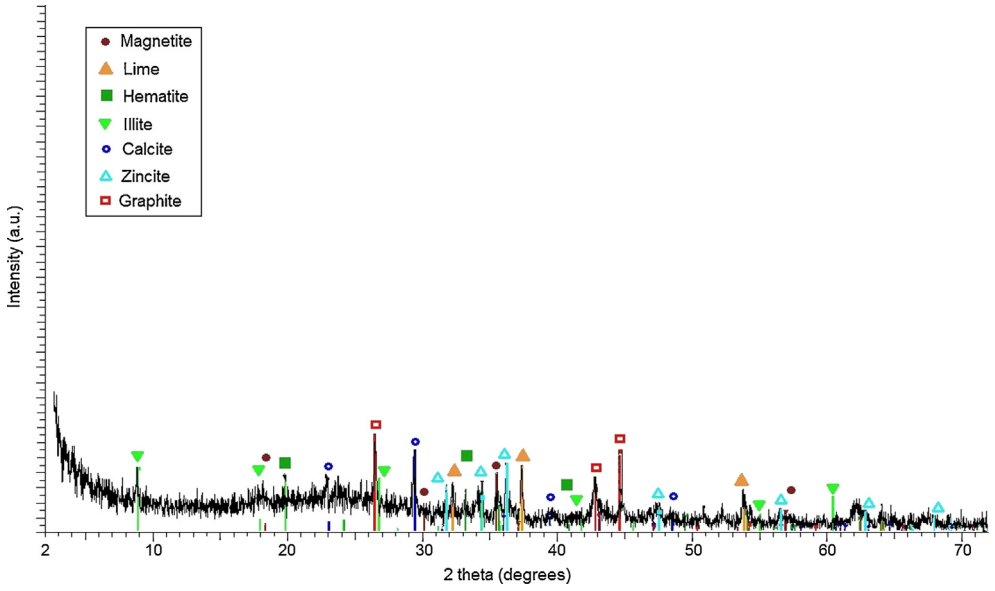

Fig. 4 – XRD of carbon and bed material.

within the bed material, avoiding their segregation after water addition.

Fig. 5 shows the weight loss and differential weight loss of the same material analyzed in Fig. 4. It is seen that the thermal decomposition of this material occurs basically at different stages. At ~200–600 °C there is a continuum loss of weight that can be attributed to oxidation of the organic matter (pyrolyzed or unburned material) coming from the sawdust. At 600–750 °C the loss of weight and the appearance of a peak in DTG can be attributed to breakage of carbon sp^2 bonds [18], and the oxidation of amorphous carbon both becoming carbon mono/dioxide. Precisely, Kakade [18] attributed the decomposition of SWNT in 400–600 °C, whereas Zhou [19] found the decomposition of MWNT in 750–850 °C. At ~750 °C begins the calcination of calcite, and also some oxidation and byproduct formation from the reducing agent and the catalyst.

3.2.2. *Characterization of carbon fibers (CF) and nanotubes (CNT)*

In Fig. 6, the growing of CF/CNT can be observed on the catalyst particles. Fig. 7 shows carbon structures with a large aspect ratio. The micrographs indicate the presence of CF and CNT with different morphologies, varying in size and thickness (Fig. 7). The sample was not purified, and then part of the bed material appears in the micrographs.

The carbonaceous material can be purified using a process involving mild heat treatment followed by alkali and/or acid treatments [15], but further investigation is necessary. For application in concrete it may not be necessary.

Fig. 8A–D shows images of CNT/CF observed in transmission electron microscopy (TEM) as presented in SEM images (Fig. 7). The images show materials with a minimum thickness of approximately 25 nm, what is straightforwardly seen

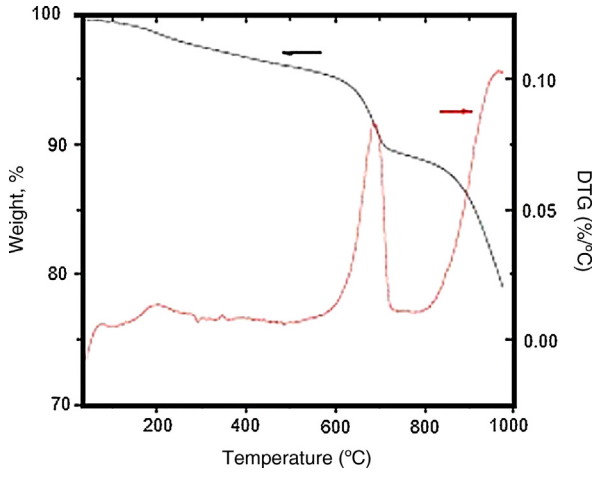

Fig. 5 – TGA/DTG of carbon and bed material calcined in air atmosphere up to 1000 °C.

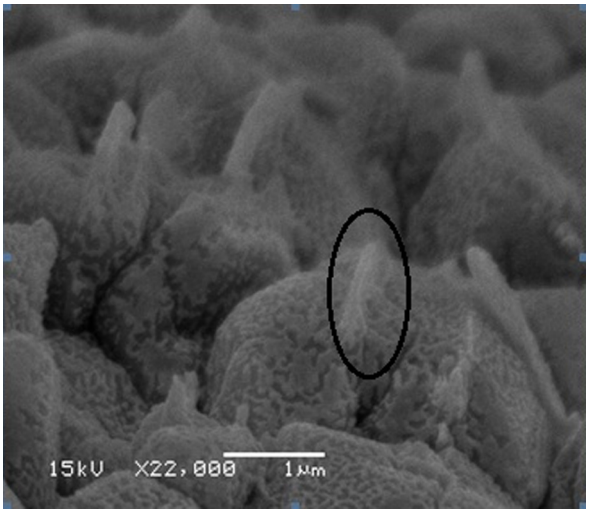

Fig. 6 – SEM of nanofibers/CNTs growing on the bed material.

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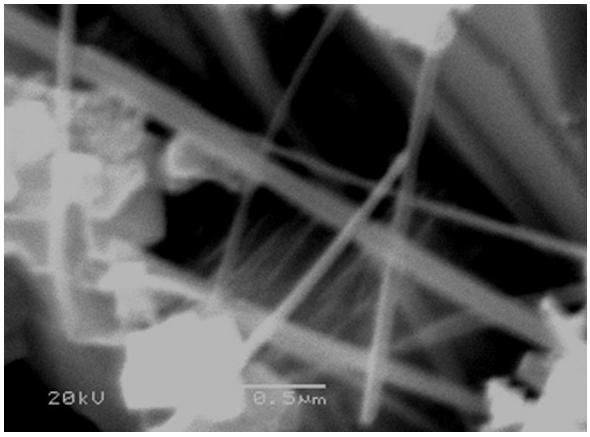

Fig. 7 – SEM of carbon fibers and CNTs. Thinner tubes can be seen on second plan.

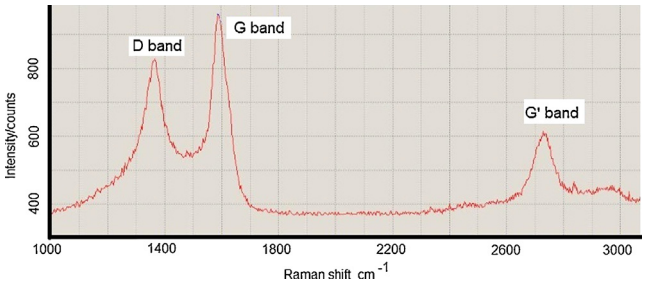

Fig. 9 – Raman spectra of the characteristic bands of nanofibers and CNTs.

in Fig. 8C. Although a hollow morphology is not clear, nanotubes are usually associated with nanoscale dimension. It can be concluded that the method used in the synthesis allows obtaining nanocarbon materials of varying thicknesses, but finer than 50 nm (Fig. 8A–D). Furthermore, in Fig. 8D, probably bundles of carbon nanotubes can also be presented, formed by single and double walled carbon nanotubes with very fine diameters. In general, it is possible to observe nanomaterials with high aspect ratio (*L*/*D*) which is an important feature for future applications, especially for toughness improving of materials such as polymers and construction concretes.

The method showed in this work demonstrated that the production of CNT/CF is promising. Nonetheless, these CNT/CF present considerable amounts of defects, such as circumference-type, point-type, and groove-type as proposed in Zhou's work [19]. In addition, it can also be noted strong variation in size and thickness of the materials. This can be a consequence of the production process from a residue such as sawdust. However, a higher control of processing/reactor parameters, and CNT/CF purification step, can lead to a considerable improving in the quality of the carbon nanostructures.

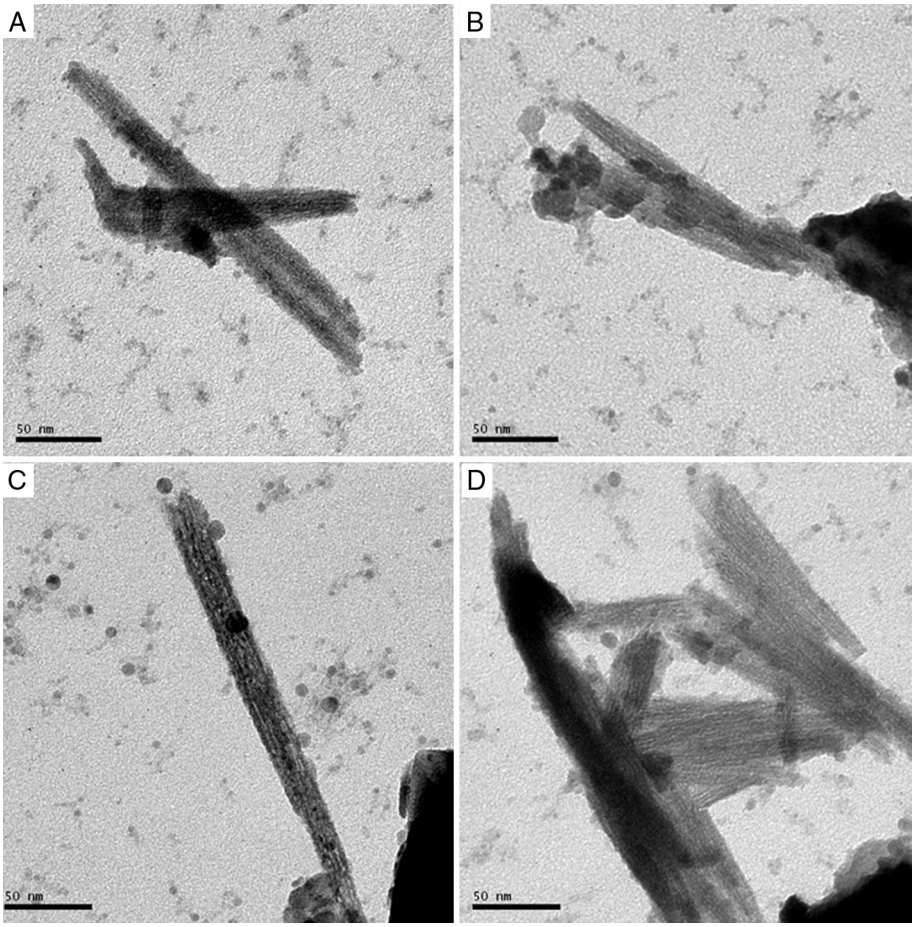

Fig. 8 – TEM of nanofibers and CNTs.

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Raman spectroscopy of the samples was used in order to study the quality and the yield of carbon nanostructures. It can be seen in Fig. 9 three distinctive peaks located at approximately 1365, 1590, and 2740 cm^{-1} that are usually found in Raman spectra of nanotubes [15,18,20]. The two strong peaks centered at 1580 and 2700 cm^{-1}, G and G′ bands, respectively, are typically referred to graphite [21]. The G band is associated to perfect nanotubes and the other peak, named D band is associated to presence of disordered structures, such as CNT with flaws, and non-crystalline carbon.

The Raman analysis confirms what was showed previously in Fig. 8 (TEM analysis). The size of D band in Fig. 9 is significant and point out CNTs with low crystallinity and presence of flaws in the structure, as mentioned before.

The quality of the nanotubes can also be related to $I(D)/I(G)$ ratio (this was shown to be excitation laser energy dependent which is only a comparative criterion [21] which was lower than 1 ($I(D)/I(G) = 0.72$), and this indicates that the CNT are well graphitized. This is a good result considering the experimental conditions, and absence of a purification method. For comparison, typical commercial multi-wall carbon nanotubes have shown a ratio of 1.79 [22]. However, it must be inferred that G and D bands (Fig. 9) represent different peak intensities with wide peak compared to commercial CNTs, what means CNTs with impurities.

4. Conclusions

From the results obtained in this work, the following conclusions can be drawn:

- Tests conducted in the designed reactor attest to the possibility of producing nanocarbon materials of eco-friendly and cost-effective way. The synthesis of carbon fibers and nanotubes through the pyrolysis of wood sawdust was a viable process. In this process hydrogen can also be produced, and low pollutant gases emissions. A low temperature 750 °C was needed to the formation of CNT/CF.
- The thermodynamic simulations were a successful way to predict the ideal experimental conditions to the synthesis of hydrogen and carbon, and to reduce the emissions of the gases CO_2, CO and CH_4 in the atmosphere.
- Graphite formation was indicated in XRD study, and the thermal analysis presented a decomposition range typical of carbon oxidation.
- SEM and TEM micrographs showed particles with high aspect ratio, with a thickness thinner than 50 nm, which are typical of carbon nanofibers and CNTs. The presence of nanocarbon materials was also confirmed by Raman analysis. They showed variation in size and thickness, with defects and flaws. However, the quality of the CNT/CF was fair enough to the study and many industrial applications. The products, i.e., CNTs/CFs within the bed, may find application in construction concrete without purification due to the compatibility between the materials.

Conflicts of interest

The authors declare no conflicts of interest.

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