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PRODUCTION OF BAMBOO-TYPE CARBON NANOTUBES DOPED WITH NITROGEN FROM POLYAMIDE PYROLYSIS GAS

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Highlights

- The viability of the bamboo-type carbon nanotubes production from pyrolysis gas by a simple process of catalytic chemical vapor deposition is demonstrated.
- The pyrolyzed polymer polyamide 6.6 provided the necessary carbon, nitrogen and hydrogen.
- Good quality nanotubes were obtained with 5 to 20 layers and 20 nm in diameter.
- The best results were obtained from pyrolysis at 900 °C and growth at 750 °C.

Abstract

Bamboo-type carbon nanotubes (BCNTs) doped with nitrogen were produced by catalytic chemical vapor deposition from the effluent gases resulting from pyrolysis of polyamide 6.6. This polymer provides the carbon and nitrogen source and allows to obtain enough hydrogen during its decomposition for the carbon nanotubes (CNTs) production without prior catalyst reduction. The influence of pyrolysis and growth temperatures was studied in order to obtain the best quality CNTs. Transmission electron microscopy, X-ray diffraction, and Raman spectrometry showed that the best results were obtained at 900 °C pyrolysis temperature and 750 °C growth temperature, since the presence of amorphous carbon was negligible and the best crystalline degree was obtained. These BCNTs had from 5 to 20 layers and their arcs of bamboo-like compartments had from 3 to 15 layers. They had 20 nm in diameter and lengths typically on the order of micrometers.

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Keywords: BCNTs; chemical vapor deposition; polyamide 6.6; pyrolysis

1. Introduction

Carbon nanotubes (CNTs) were first reported by Oberlin et al. [1] and were extensively studied after the profound characterization given by Iijima [2], due to its extraordinary mechanical and conductive properties. They are graphitic materials composed mainly of carbon, where the basic units are graphene layers rolled into perfect cylinders. However, there are also CNTs lattices where foreign atoms are inserted, thus modifying their structure and their chemical and physical nature. Some authors have studied CNTs doped with different heteroatoms as boron [3,4], nitrogen [5-7] and others, but among them, the bamboo-type CNTs doped with nitrogen (BCNTs), have particular interest in electronics since they show a higher electron carrier concentration that renders n-type behavior [8-12]. Therefore, the synthesis of these materials is crucial in the semiconductor industry if they want to be used as future building blocks, in nanocomposites and nanoelectronic devices. In fact, their interest is increasing in a variety of electrical engineering applications. The field emission characteristics of BCNTs have also been demonstrated to be better than those of pristine CNTs [13]. Additionally, nitrogen-doped graphitic materials present a high enhancement of the specific electrical capacitance, of great importance in energy storage [14].

Nitrogen atoms can be incorporated into the CNTs lattice through either in situ methods, using a nitrogen source together with the carbon source, or through post-treatment strategies [15]. In situ techniques are more commonly reported in recent investigations, with strategies such as dc-arc evaporation [16], thermal chemical vapor deposition (c-CVD) [17-23], and microplasma assisted CVD [24-27]. Previous research references were found for CVD synthesis methods where expensive reagents are used, and sometimes hydrogen as a reaction atmosphere. Moreover, usually they are complex methods and nitrogen-carbon precursor gas stream must be evaporated previously in order to be homogeneous before injecting it into the CVD reactor. Chen and Higgins [28] employed three different kind of mixtures of ferrocene and three different aliphatic diamines (ethylenediamine, 1,3-diaminopropane and 1,4-diaminobutane) in solution, and injected them in a furnace at 800 °C. Katayama et al. [29] evaporated Ni-phthalocyanine and grew BCNTs in two consecutive furnaces at temperatures of 600-850 °C in presence of H₂/Ar. Boncel et al. [30] made use of a mixture well dissolved of toluene and pyrazine, which decomposes into acetylene, hydrogen cyanide and cyanoacetylene at 760 °C, as

the carbon and additional heteroatomic nitrogen precursor along with ferrocene. This feedstock was introduced in a horizontal injection c-CVD furnace at temperatures of 760 and 860 °C. Wong et al. [31] synthesized BCNTs using precursor solutions which consisted of ethanol and aniline, diethylamine, and ethylenediamine, respectively. The premixed solutions were heated to its boiling point before entering the furnace along with iron (II) phthalocyanine when temperature reached 850°C. Li et al. [32] chose imidazole, as both precursor of carbon and nitrogen, and ferrocene as the catalyst, they were evaporated simultaneously and carried by Ar into a horizontal quartz tube furnace at 850°C. Villapando-Paez et al. [33] synthesized BCNTs by pyrolyzing a ferrocene/ethanol/benzylamine solution. For that purpose, the solution was first introduced inside an aerosol generator, and the mist produced was directed to a furnace operated at 950°C. Srivastava et al. [34] pretreated an iron film in NH₃ plasma and introduced acetylene and hydrogen in a tubular microwave plasma enhanced CVD at 600 °C. Lee et al. [35] produced BCNTs with a Ni/Si catalyst dipped in HF solution and treated with NH₃ and acetylene at 950 °C in a quartz reactor. Hao et al. [36] pyrolyzed acetonitrile over MgO supported Fe catalyst in a tube furnace in the presence of hydrogen at 850 °C.

On the other hand, several studies have already shown the viability of different waste plastics pyrolysis gas as a carbon source and hydrogen evolution for the production of CNTs and carbon nanofibers (CNFs). A pyrolysis stream produced in a first reactor (or first half of a reactor) is conducted to a second reactor for filament growth by c-CVD. These studies are mainly focused on the production from polyolefins, polypropylene [37-42] and polyethylene PE [42-45]. Other contribution studies the production of CNT from a mixture of waste polymers, more realistic and economically viable, which consists of a majority of polyolefins with small contribution of polystyrene [37,46], polyvinyl chloride [42,46], PET [47], etc. Borsodi et al. [46] also studied the production of CNTs from a pyrolysis stream of a set of waste polymer mixtures, including one based on polyolefins and 1 wt-% polyamide. However, nothing was reported about its structure with respect to those mixtures without a nitrogen feedstock. Consequently, there are no studies about production of BCNTs from waste polymers to our knowledge.

In view of these circumstances, the aim of this work was to take advantage of the nitrogen content in the structure of some polymers to study the feasibility to grow BCNTs by c-CVD. To this end, the effluent gases from pyrolysis of polyamide (PA) were used, thereby

avoiding extra carbon, hydrogen and nitrogen source and without prior reduction of the catalyst. Thus, the process is simplified and the cost is reduced with respect to other methods proposed in the literature. In addition to this, the influence of pyrolysis and growth temperatures was studied to find the proper conditions for the best quality of BCNTs.

2. Material and methods

2.1. Preliminary pyrolysis study at laboratory scale

As a first approximation to know the composition of the effluent pyrolysis gases of PA at different temperatures, a preliminary study of a set of polymer decomposition experiments in a bench-scale reactor was carried out. The PA used was PA 6.6 (Dinalon Natural A3S25-0042, Grupo Repol, Spain). The reactor was a batch horizontal quartz tubular furnace (AOX Euroglass 1600) where around 200 mg of polymer was pyrolyzed at different temperatures, ranging from 600 to 900 °C based on the literature [48-50]. The feeding system of the reactor allows the introduction to the sample to the oven once it is already at the setpoint temperature, which assures to reach the final temperature in a few seconds, simulating a continuous reactor. More details about the apparatus can be found elsewhere [44]. Special attention was paid to obtain nitrogen compounds and hydrogen as decomposition products, since they are required for growing BCNTs.

Gases and volatile compounds evolved in the thermal process were collected in a Tedlar® bag and analyzed by gas chromatography. On the one hand, a Shimadzu GC-14A gas chromatograph equipped with a thermal conductivity detector (TCD) was used, with a Supelco carbosieve SII (4 m x 1/8) column to value mainly hydrogen, and with a concentric Alltech CTR I column (6 ft x 1/8 in. and 6 ft x 1/4 in. for the inner and outer columns, respectively) to value mainly CO and CO₂. On the other hand, the light hydrocarbons were analyzed in a Shimadzu GC-17A gas chromatograph with a Supelco capillary Alumina-KCl Plot column (30 m x 0.32 mm) in split injection and a flame ionization detector (FID). The identification and the quantification of all the analyzed compounds were carried out with a prior external standard calibration. Moreover, these samples were analyzed by active capture of gases to know the content in NH₃ using a gas detector Industrial Scientific MX6 iBRID.

2.2. BCNTs growth from pyrolysis in pilot plant

BCNTs growth from in-situ produced PA 6.6 gases was carried out by a two consecutive reactors, a first system for producing a continuous and stable pyrolysis gas stream and a second system for the catalytic batch CVD growth of BCNTs (Figure 1). The first system consists of a continuous vertical fluidized bed reactor externally heated of 36 mm diameter and 420 mm long. Extruded PA 6.6 is fed through a vibrating system at 3 g min^{-1} . A nitrogen flow of 8 mL s^{-1} , passing first through a preheater consisting of two concentric cylinders, assures the fluidization of the sand bed ($d_p = 105\text{-}297 \text{ }\mu\text{m}$) and supposes a minimum contribution to the gas production. The effluent gas exits the first system through the top side and passes through a condenser system before the second reactor. Gas portions were sampled through a septum valve located after the condenser system at different intervals of time, to check the composition of the stream and the reproducibility.

The growth reactor is a quartz tubular reactor, 30 mm ID and 300 mm length, controlled by an electric heater. Prior to the pyrolysis run, a catalyst precursor was introduced first in a crucible so BCNTs can grow by the CVD substrate method after starting the run.

First reactor (pyrolysis)

Figure 1. Diagram of the experimental set-up used for the BCNTs synthesis

2.2.1. Catalyst preparation and characterization

An in-house produced catalyst consisting of Fe/Al₂O₃ was used. It was prepared by the co-precipitation method [51]. Al(NO₃)₃·9H₂O aqueous solution at 1 wt-% was mixed with Fe(NO₃)₃·9H₂O solid up to an atomic ratio Fe:Al of 1:2.5 was reached. Afterwards, Na₂CO₃ aqueous solution of concentration 1 mol L⁻¹ was added until pH 7.0 was achieved. The resulting precipitate was filtered, washed, dried at 108°C for 24 h and subsequently calcined at 450°C for 8 h soaking time to obtain Fe₂O₃/Al₂O₃. The catalyst was manually crushed in a mortar before its use.

The characterization of this catalyst was evaluated in a previous study by transmission electron microscopy (TEM), X-ray fluorescence and scanning electron microscopy (SEM) employing electron dispersion spectroscopy (EDS). Details can be consulted elsewhere [44]. The results showed that the catalyst was satisfactorily synthesized, where Fe was well dispersed over the Al₂O₃ support, and that the Fe₂O₃ nanoparticles size distribution was in a range on the order of 2 nm.

2.2.2. BCNTs production

0.1 g of the calcined catalyst precursor was first placed in a crucible inside the growth reactor. Furthermore, both consecutive reactors were first heated to target the temperatures under a nitrogen flow of 8 mL s⁻¹. Then, PA 6.6 was fed continuously to the first reactor for 40 min. Exhaust gases samples from the pyrolysis reactor were collected in a Tedlar® bag at 20, 30 and 40 min and they were analyzed by gas chromatography as commented in section 2.1. No extra hydrogen was fed, so the hydrogen formed from pyrolysis was the only one present for reducing the catalyst and having the necessary reducing atmosphere. After 40 min of BCNTs growing, the system was cooled down to room temperature under a nitrogen flow.

Table 1 shows the series of experiments performed at different pyrolysis temperatures in the range between 700 and 900 °C, based on results obtained in experiments of section 2.1, and nanotubes growth temperatures between 700 and 750 °C based on previous data [44].

The morphologies of the graphitic products were examined by TEM using a JEOL JEM-2010 instrument operated at 200 kV. Prior to imaging, the samples were dispersed in isopropanol in an ultrasonication bath and dropped onto copper grids covered with a carbon film. The purity and phase structure of the as-prepared products were characterized by Raman spectroscopy with a Jobin-Yvon LabRam spectrometer equipped with a confocal microscope and employing a He-Ne laser of 633 nm as the exciting radiation. The purity was also studied by thermogravimetric analysis (TGA) using a METTLER TOLEDO TGA/SDTA851e/SF/1100 instrument operating under air with a heating rate of 10 °C min⁻¹. The nature of the superficial groups and the atomic surface elemental composition were carried out by X-ray photoelectron spectroscopy (XPS) employing a Thermo-Scientific K-Alpha. This equipment has connected a prior high vacuum chamber where the samples pass before being analyzed to remove the greatest portion of absorbed carbon due to air contamination. A survey scan was performed from 1200 to 0 eV on each sample, followed by a narrow scan specifically on the C1s, N1s and O1s regions.

3. Results and Discussion

3.1. Preliminary pyrolysis study at laboratory scale

Figure 2 shows the gas composition for the experiments from 600 to 900 °C as a function of pyrolyzed polymer mass. At low temperatures, the yield of light hydrocarbons up to five carbon atoms (those determined by GC-FID) was low, since mainly oligomeric fragments and monomeric units were obtained according to the literature [48], which mainly go as condensed liquids. The fragment adipic acid presents a tendency to undergo cyclization, and cyclopentanone is considered as the principal product obtained from pyrolysis at 550 °C. Upon high temperature pyrolysis (530-800 °C) in vacuum, PA 6.6 gives amines, amides, nitriles and hydrocarbons [52]. The major components of the noncondensable effluent gas obtained from PA 6.6 decomposition were the light hydrocarbons methane, ethylene, ethane, propylene, and benzene, as well as hydrogen. Toluene was also a major component but to a lesser degree. In addition, due to oxygen and nitrogen atoms in PA 6.6 structure, carbon oxides and NH₃ were formed to a considerable share. The total amount of these compounds reaches at least 86 vol % of the noncondensable products based on nitrogen-free gas for all experiments. The rest up to

100% corresponds to other hydrocarbons such as acetylene, butane, 1-butene, cis-2-butene, 1-pentene or hexane, among others.

It is notable that the hydrogen concentration increased with the pyrolysis temperature. The amount of ethylene and propylene, which are hydrocarbons that decompose easier at medium temperatures, [44,53,54] increased with rising the pyrolysis temperature although propylene had the highest ratio at 800 °C and decreased after this temperature. NH_3 yield varied around $0.5 \text{ mmol g}^{-1} \text{ PA 6.6}$ ($8.5 \text{ mg g}^{-1} \text{ PA 6.6}$). However, the nitrogen content in the polymer is 10.8 % by mass according to the elemental analysis. This discrepancy is due to other different nitrogen compounds evolved in the pyrolysis at 850-900 °C, such as 3-butenenitrile, pentane to octane nitriles, hexanedinitrile and benzonitrile [49]. In relation to other hydrocarbons of limited relevance to CNT growth, as methane, ethane and aromatic compounds, they follow trends according to the literature [53-57]. The methane quantity increased with the pyrolysis temperature. The ethane amount was less significant and had its highest ratio at 750 °C. Regarding the benzene and toluene composition, they did not reach important concentrations. It can be seen that carbon oxides increased significantly from 600 °C to 750 °C and remained approximately constant until 900 °C in accordance with the study of Braun and Levin [48]. The composition of the pyrolysis gas depends on the relative formation of each compound. At 900 °C, the cracking reactions take place in large extension and then produce a large evolution of methane and hydrogen. Consequently, the relative concentration of the other components decreases with respect to them, although some compounds still present appreciable values, such as ethylene and carbon monoxide.

As reported in a previous study [44], olefins are much more reactive for yielding CNTs than paraffins. Thus, the pyrolysis temperatures for the subsequent study of growing BCNTs were selected for maximizing the ethylene and propylene amounts as well as H_2 required. Nevertheless, the analysis of the presence of carbon oxides is also important. When feeding CO and CO_2 into the growth reactor at low quantities, better crystalline degree is achieved [58]. On the other hand, a small addition of CO with an ethylene and hydrogen mixture can improve the CNT yield, but if the CO concentration increases, the yield decreases [59,60]. This indicates that certain amount of carbon oxides is favorable if it is kept a good proportion of hydrogen and hydrocarbons. Therefore, sets of pyrolysis of PA 6.6 at 700 °C, 800 °C and 900 °C were selected for the subsequent study of growing BCNTs.

Figure 2. Yields of major components of the noncondensable effluent gas obtained from PA 6.6 pyrolysis in laboratory study

3.2. BCNTs growth from pyrolysis in pilot plant

3.2.1. Pyrolysis gas composition

Figure 3 shows the average values of composition of the pyrolysis gases collected at 20, 30 and 40 minutes of plant operation, and adjusted to 100 vol % with the major components for the different pyrolysis temperatures studied in pilot plant. As can be observed, hydrogen, ethylene and methane are the compounds with the highest proportion. In addition, these gaseous compositions followed the same behavior as that obtained in the laboratory study. Ethylene, propylene and NH₃ had their highest concentration at 800 °C. Hydrogen and methane ratio increased with temperature. Carbon oxides percentage fluctuated slightly. As for the laboratory experiments, the small amount of NH₃ obtained in comparison to the nitrogen content of the polymer is remarkable, due to the presence of other nitrogen compounds. In addition, the NH₃ content decreased at 900 °C, probably as a consequence of the greater emission of other compounds at this temperature, that causes a dilution effect for NH₃. This explanation is consistent with that observed by Leichtnam et al. [50], who studied fast pyrolysis of polyamide at high temperature, observing that the formation of ammonia is similar at 800 °C than at 1000 °C. These authors also observed formation of HCN in addition to NH₃ from pyrolysis of

PA 6.6 at 800-1000 °C, in the same range for the two compounds, so the atmospheres in both pyrolysis step and growth reactor must be controlled for the safety of the process.

Figure 3. Average values of major components of the product gas from PA 6.6 pyrolysis in pilot plant (adjusted to 100 vol % by excluding the nitrogen content). Error bars show the standard deviation

3.2.2. BCNTs characterization

The morphologies of the tubes observed by TEM clearly indicated a BCNT structure formed because of the presence of NH₃ in the pyrolysis gases stream, since this compound favors this kind of nanotubes [61-72]. Nitrogen inclusion contributes to the reduction of tube diameters because it promotes the formation of pentagons into sp² net, due to its delivery of higher energy stability [73] or due to the increase of surface defects which causes twist layers and close it [74,75].

Figure 4 shows TEM micrographs of samples produced at different pyrolysis and growth temperatures. At a growth temperature of 700 °C, CNTs present a short crystalline order, has no periodic arrangement, and therefore the structure was difficult to elucidate. These structural defects are more evident when pyrolysis was carried out at lower temperatures, whereas from pyrolysis gases at 900 °C the walls are straighter and reveal fewer defects. At 720 °C, the CNTs crystallinity slightly enhanced, however a slight amorphous carbon coating appeared, which was greater when pyrolysis temperature was 700 °C. Lastly, at 750 °C growth temperature, the lower pyrolysis temperature, the greater the presence of external amorphous carbon coating, and only soot was obtained at 700 °C pyrolysis

temperature. Thus, as can be observed the pyrolysis temperature was critical. At 900 °C pyrolysis temperature the presence of amorphous carbon was always negligible and the best crystalline degree was obtained at 750 °C growth temperature. Figure 5 showed that these BCNTs had from 5 to 20 layers and their arcs of bamboo-like compartments had from 3 to 15 layers. They had lengths typically on the order of micrometers and the diameter distribution histogram (Figure 6), obtained by counting 100 BCNT diameters, confirmed that it was in a range on the order of 20 nm.

Figure 4. TEM images of BCNTs of the experiments at different pyrolysis and growth temperatures

Figure 5. TEM images of BCNTs of the experiment at 900 °C pyrolysis and 750 °C growth temperatures

Figure 6. Diameter distribution histogram

Raman spectroscopy results are shown in Figure 7. The heteroatoms are defects in the sp^2 structure, thus spectra provide information on the extent of disordering and changes in the electronic structure. All of them are very similar and typical of functionalized

materials and present, in agreement with Chizari et al. [76], wide bands, nonexistent or low intensity 2D-peaks and high inflexion points between D and G-bands.

At 700 °C and 800 °C pyrolysis temperature D and G-peaks present similar intensities at different growth temperatures. Moreover, both pyrolysis temperature spectra exhibit a wide D-band due to a shoulder at 1100 cm^{-1} which corresponds with I-band, also denoted as D4-band, associated with disordered graphitic lattice and presence of nitrogen and oxygen molecules intercalated between the nanotube layers [77,78]. Nevertheless, it can be observed that the I-shoulder is more important in samples grown at 750 °C, which could be attributed to an increase of amorphous carbon when rising the growth temperature, as observed in TEM exploration. At 900 °C pyrolysis temperature it can be observed that width at half-height D-peak is thinner than at lower pyrolysis temperature. It has less contribution from I-shoulder.

Moreover, D-peak intensity is higher at high growth temperature and at 750 °C it can be observed a more stylized peak. This indicates an improvement of the crystalline degree with higher pyrolysis and synthesis temperatures, due to wax creation at lower pyrolysis temperatures. Therefore, the BCNTs with the best quality were, in agreement with TEM, those obtained at 750 °C with pyrolysis gases at 900 °C.

Figure 7. Raman spectra of BCNTs of the experiments at different pyrolysis and growth temperatures

The TG and DTG profiles of the best quality samples according to TEM and Raman spectroscopy are shown in Figure 8, which are the CNTs obtained from pyrolysis gases at 900 °C. The main weight loss corresponding to the experiments at growth temperatures of 720 and 750 °C were very similar, almost vertical, whereas that corresponding to the

experiment at 700 °C presented some angle with respect to the vertical axis. Therefore, the oxidation peak with the largest full width at half-maximum observed in DTG results was that belonging to 700 °C, which corresponds to the lowered order CNTs, as shown through TEM explorations. In addition, the temperatures of the onset of the oxidation weight loss and the maximum oxidation rate are different in these three samples. According to the literature [30,76], temperatures are lower than those of MWCNT, due to the higher number of defects in their structure caused by heteroatoms introduced, making them less resistant to oxidation. In DTG curves it can be seen that different oxidation peaks were moved to higher temperatures in this order: 720 °C, 700 °C y 750 °C. An increase in the oxidation temperature means a higher thermal stability and an improvement in crystallinity [76,79,80], which in this case follows this order of growth temperatures. In this way, the same conclusion is drawn as with the previous techniques, BCNTs growth at 750 °C from pyrolysis carried out at 900 °C are the most graphitic and crystalline ones.

Figure 8. TG and DTG curves of BCNTs of the experiments realized by pyrolysis at 900 °C and different growth temperatures. Carbon reaction yield of BCNTs per catalyst mass for these samples are 0.722, 1.916 and 0.663 g of carbon/g of catalyst for 700, 720 and 750 °C growth temperatures respectively

Figures 9 and 10 show the XPS pattern with relation to C1s, O1s and N1s peaks. Specifically, only C1s (Figure 9) and N1s (Figure 10) regions and their deconvolutions are shown, because O1s peak is disrupted due to alumina present into the catalyst. To gain further insight into the morphologies of the nanotube structures, the C1s region was deconvoluted to provide a quantitative view of the configurations in the nanotubes. The three samples exhibited similar C1s chemical environments, as demonstrated in Figure 9. They showed that the aromatic C=C bond (binding energy of 284.5 ± 0.2 eV [81-84]) is much more important than others oxygenated configurations. In addition, binding energy of C=N bond is located between 285.7 eV and 286.3 eV [81,85,86], so it is possible that these bonds can be overlapped with epoxy groups or hydroxyl and C-C sp³ bonds.

Figure 9. XPS spectra of C1s in BCNTs of the experiments realized by pyrolysis at 900 °C and growth at (a) 700 °C, (b) 720 °C and (c) 750 °C

To get insight to the bonding environment of nitrogen, the deconvolution of N1s peak was carried out and the result is shown in Figure 10. The N1s spectrum of these BCNTs consists of three distinct peaks located at various binding energies: pyridinic-N-oxides (binding energy of $402 - 405 \pm 0.2$ eV), quaternary-N (binding energy of $401.1 - 401.8 \pm 0.2$ eV) and pyridinic-N (binding energy of 398.6 ± 0.2 eV) [87-89]. The quaternary-N corresponds to nitrogen species that replace carbon into the lattice, so as can be seen, the most resistant to higher temperatures and the most abundant in three samples, which is in accordance to the study of Chizari et al. [76]. Furthermore, when growth temperature increased to 720°C, pyridinic-N-oxides proportion was increasingly higher.

Figure 10. XPS spectra of N1s in BCNTs of the experiments realized by pyrolysis at 900 °C and growth at (a) 700 °C, (b) 720 °C and (c) 750 °C

On the other hand, Table 2 shows the nitrogen content analysis of all samples. The overall nitrogen composition was always greater than 3 wt %. Although it varies relatively little, when rising the synthesis temperature, the overall percentage of nitrogen incorporated into the BCNTs structure decreased. This trend can be attributed to several causes in agreement with the literature. The study of Chizari et al. [76] deduced that the lower number of defects and higher crystallinity of the BCNTs synthesized at higher temperatures, make difficult the acceptance of foreign elements into the structure. Liu

and his co-workers [90] related that to the fact that the C-C bonding energy (370 kJ mol^{-1}) is higher than the C-N bonding energy (305 kJ mol^{-1}), thus the formation of the C-C bonding is expected to be more favorable at higher temperatures. Terrones et al. [91] attributed this phenomenon to the fact that at high temperatures, stable N_2 molecules can also be formed and will no longer constitute part of the BCNTs structure. Van Dommele et al. [92] reported that the easier formation of iron carbides compared to iron nitrides on the catalyst at higher temperatures, leads to the lower participation of nitrogen in the BCNTs structure.

Finally, this technique is the only one that confirms the presence of nitrogen atoms into the BCNTs surface, which causes defects in the structures and makes them less resistant to oxidation [30,76], as can be concluded by TGA.

Summarizing, the best BCNTs are obtained at 750°C from PA 6.6 pyrolysis gases at 900°C . From pyrolysis at 900°C , the amount of heavy hydrocarbons and semivolatile compounds obtained in the effluent stream and corresponding to wax is very small, so with a synthesis at 750°C , the best crystalline quality and no soot is obtained.

4. Conclusion

Good quality nitrogen doped BCNTs were directly synthesized from a polyamide pyrolysis gas stream. The synthesis was carried out on an iron catalyst supported on alumina by the CVD method from direct pyrolysis gases of a polymer with functional groups in its structure, PA 6.6. This gaseous stream was generated in a continuous process in a fluidized bed reactor at pilot plant scale. The effluent gas from PA 6.6 pyrolysis has, as well as light hydrocarbons and enough hydrogen, NH_3 and carbon oxides, due to presence of nitrogen and oxygen in its structure. This gaseous composition has enough hydrogen to reduce the transition metal catalyst, and nitrogen to grow BCNTs by bending of their layers and formation of bamboo-like compartments. The crystalline quality of the BCNTs growth can be controlled by the operating conditions. The most crystalline BCNTs corresponded to the highest temperatures of pyrolysis and synthesis, due to the small quantity of waxes and heavy hydrocarbons generated which means no amorphous carbon cover. The higher the growth temperature, the lower the nitrogen content into the BCNTs structures. Therefore, the proposed process is sustainable and economical with respect to hydrogen and nitrogen, since it is not necessary to add more than that provided

by the pyrolysis of PA 6.6. A high added value product is obtained from a waste with a simple and environmentally friendly method.

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Figure captions

Figure 1. Diagram of the experimental set-up used for the BCNTs synthesis

Figure 2. Yields of major components of the noncondensable effluent gas obtained from PA 6.6 pyrolysis in laboratory study

Figure 3. Average values of major components of the product gas from PA 6.6 pyrolysis in pilot plant (adjusted to 100 vol % by excluding the carrier nitrogen content). Error bars show the standard deviation

Figure 4. TEM images of BCNTs of the experiments at different pyrolysis and growth temperatures

Figure 5. TEM images of BCNTs of the experiment at 900 °C pyrolysis and 750 °C growth temperatures

Figure 6. Diameter distribution histogram

Figure 7. Raman spectra of BCNTs of the experiments at different pyrolysis and growth temperatures

Figure 8. TG and DTG curves of BCNTs of the experiments realized by pyrolysis at 900 °C and different growth temperatures. Carbon reaction yield of BCNTs per catalyst mass for these samples are 0.722, 1.916 and 0.663 g of carbon/g of catalyst for 700, 720 and 750 °C growth temperatures respectively

Figure 9. XPS spectra of C1s in BCNTs of the experiments realized by pyrolysis at 900 °C and growth at (a) 700 °C, (b) 720 °C and (c) 750 °C

Figure 10. XPS spectra of N1s in BCNTs of the experiments realized by pyrolysis at 900 °C and growth at (a) 700 °C, (b) 720 °C and (c) 750 °C

Figr-1

Figr-2

Figr-3

Figr-4

Figr-5

Figr-6

Figr-7

Figr-8

Fig-9

Figr-10

a.

b.

c.

Table 1. Experiments of BCNTs growth carried out

Experiment	Pyrolysis	Growth	
	T (°C)	Prior Reduction	T (°C)
700+700	700	No	700
700+720		No	720
700+750		No	750
800+700	800	No	700
800+720		No	720
800+750		No	750
900+700	900	No	700
900+720		No	720
900+750		No	750

Table 2. Nitrogen content of the synthesized BCNTs from PA 6.6 pyrolysis gases by XPS

Experiment	% N
900+700	4.25±0,22
900+720	4.02±0,28
900+750	3.03±0,20