Agro-industrial Waste as Precursor Source for Carbon Nanotubes (CNTs) Synthesis Using a New Technical of Solvent Autoignition

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Abstract. The objective of this research was to evaluate a novel technique of synthesis by solvent autoignition. The CNTs were synthesized using two methods of solvent autoignition: radiation assisted by a microwave oven and autoignition by muffle-furnace. Synthesized CNTs were examined by dynamic light scattering, UV-VIS spectroscopy, and Raman spectroscopy. The results indicate that the physicochemical properties of CNTs were influenced by synthesis method. Biochars obtained by autoignition through the muffle-furnace produced higher CNTs concentration and smaller hydrodynamic diameter and show a higher degree of wall graphitization, suggesting superior CNT quality. These results are promising for application in the construction industry and as a sustainable lignocellulosic residual biomass management solution.

1. Introduction

Carbon nanotubes (CNTs) are materials of increasing interest due to their excellent electronic properties as well as their physical and chemical properties. CNTs have been used in a variety of industrial sectors as a filler material in composites to improve mechanical properties or electrical conductivity [1-3]and they have been synthesized with various techniques such as laser ablation, electric arc discharge, and chemical vapor deposition. These methods produce CNTs with different characteristics, involving complex experimental setups adding cost of production, as they require expensive processing conditions including gases as feedstock, high vacuum levels, high temperature, inert atmosphere, and they present long processing times[2].

Currently, new techniques for the selective synthesis of CNTs have been explored, such as the use of microwave radiation due to its advantages, for instance, volumetric heating, rapids reaction time

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over other conventional heating methods[4-7]. Moreover, a method of nanotube synthesis using solvent autoignition as a new strategy for CNTs synthesis has been studied[8]. In this method biochar is utilized as a source of black carbon for CNTs production, being able to produce large quantities of purified carbon nanotubes.

Biochar is a carbon-rich porous material obtained by the pyrolysis of biomass and that can be used as precursor material for CNTs growth[4]. The pyrolysis process employed to transform these materials chemically, is an alternative to biomass valorization processes, as the waste can be managed more suitably which can increase sustainability in the manufacturing industries. It has been reported that biochar application to soil increases the soil organic carbon, improves water holding capacity and soil aeration, increases the cation exchange capacity, neutralizes the pH of acidic soils, improves the soil microbial ecology and increases the specific surface area [9, 10]. Moreover, biochar can be used as a sustainable alternative in the biomass valorization for added value product production such as adsorbent of ammonium, nitrate[11], cadmium [12], phenols [13], production of silicon compounds and fulvic acids[9], among others.

Biochar has been receiving attention due to its potential importance in agronomic and environmental applications[10]. Recently, its use as precursor material for CNTs growth has been evaluated due to the potential decrease in manufacturing costs in microwave-assisted synthesis using biochar and ferrocene as catalysts[4]. This method is favored as it reduces the overall consumption of raw materials and there is no need for a source of pure carbon for CNT synthesis.

Recently, CNTs have been extensively studied as a reinforcement material for cement-based composites. The growing interest is to modify the cement matrix taking advantage of the outstanding properties of CNTs [14]. CNTs are suitable candidates for cement reinforcement, being potentially able to retain the propagation of small nano-cracks and improve the low tensile strength and low strain capacity. In addition, the improvement the fracture properties and early age strain capacity of cement pastes and mortars, reducing or preventing crack initiation are improved [15]. Cement reinforcement with CNTs has presented sensitive and stable responses to repeated compressive loadings and impulsive loadings[16], having thus a great potential of application in the construction industry.

In this research we evaluated CNTs production using biochar as the biological precursor in nanotube synthesis using a solvent autoignition method, which could be a promising route to reduce CNTs production cost and a sustainable lignocellulosic residual biomass management solution.

2. Methodology

2.1. Materials

Agroindustrial waste from plantations in Southern Chile such as wheat straw, oat hulls, rapeseed cake and hazelnuts hulls were selected for this study and used as carbon precursor. The characterization of the feedstock is shown in Table 1.

Table 1. Proximate and ultimate analysis for wheat straw, oat hulls, rapeseed cake and hazelnuts hulls feedstock used in experimental work [4]

Feedstock	Fixed Carbon (%)	Volatile matter (%)	Ash (%)	Moisture (%)	N (%)	C (%)	H (%)	S (%)	O (%)
Oat hulls	16.94	69.02	1.21	12.83	1.33	43.23	6.26	ND	49.17
wheat straw	16.11	70.41	4.75	8.61	0.63	43.11	5.81	ND	50.45
Rapeseed cake	17.37	71.7	4.17	6.51	4.67	39.42	6.18	ND	49.73
Hazelnuts hulls	37.32	51.7	1.37	8.89	0.11	35.98	6	ND	57.91

2.2. Experimental setup and procedure

2.2.1. Pyrolysis of biomass

The biomass was converted to char using a slow pyrolysis process. During pyrolysis experiments, 100 g of biomass sample was placed inside of a laboratory scale fixed bed reactor which was heated by electric resistances. The pyrolizer was operated under atmospheric pressure with heating controlled by a Data Acquisition Instrument. The pyrolysis of the samples was carried out at 600°C according to Hidalgo et al (2019)[4]. The temperature ramp rate for the reactor was of 3°C min^{-1} and the reactor was continuously injected with nitrogen (1000 ml min^{-1}) to remove the gases (volatiles) and tars produced during pyrolysis. Once the desired temperature was reached the residence time of the biomass in the pyrolyzer was approximately 3 h to ensure a complete conversion. Then, the char was separated and stored in a desiccator.

2.2.2. Synthesis of CNTs

The synthesis of CNTs was produced at solvent self-ignition temperature (SIT). The solvent used was hexane with known self-ignition conditions (SIT: 223-233°C)[17].

Feedstock converted to char was mixed with the solvent and placed in a sealed chamber under vacuum (1 Bar) in a horizontal furnace and microwave oven.

The temperature of the chamber was increased to bring the mixed char-solvent to auto-ignition condition. The energy released from the ignition produces carbon nanotubes from the char. Then, the chamber was allowed to cool down to room temperature. The sample was then taken and stored for its subsequent evaluation.

2.3. Analytical techniques

2.3.1. Characterization of CTNs

The particle size distribution of the dispersed CNTs was determined by dynamic light scattering (DLS, Zetasizer Nano S, Malvern Instr., UK). The optical properties were analyzed by UV-VIS spectroscopy (Genesis 10S UV-VIS spectrophotometer, Thermo scientific). The crystal structure was checked using Raman spectroscopy using NTEGRA Spectra spectrometer (NT-MDT, Russia) with a red monochromator of 633 nm laser excitation source.

3. Results and discussion

3.1. *Particle size distribution*

Particle size distribution was measured by DLS measurement. According to results (as shown in Table 2), a slight variation with synthesis method was observed. However, a lower hydrodynamic diameter was observed when wheat straw biochar was used in a horizontal furnace.

Table 2. Hydrodynamic diameter of CNTs

CNTs	**Horizontal furnace**	**Microwave oven**
Oat hulls	300	225
wheat straw	90	220
Rapeseed cake	180	190
Hazelnuts hulls	280	290

3.2. Optical properties

CNTs were analyzed by UV-VIS spectroscopy and showed a maximum peak of absorption around 230-250 nm. According to the results, the well-dispersed individual CNTs exhibits maximum absorption between 200 and 300 nm [18-20]. Figure 1 (a, b) shows the absorbance spectra of the CNTs synthesis in the horizontal furnace and microwave oven. In the UV region, at around 240 nm, one unique band is observed due to plasmon resonance of free nanotubes π electrons of CNTs [21]. Moreover, CNTs concentration measurement can be evaluated from Beer–Lambert's law, which establishes that the absorbance is directly proportional to the concentration [22]. Thus, a higher CNTs concentration in the synthesis by solvent self-ignition temperature,was obtained in the horizontal furnace and using oat hull biochar. Furthermore, the intensity of the absorption peak was higher, when used oat hull biochar and lower with rapeseed cake biochar. It is possible that the amount of energy released generated from the auto-ignition solvent in the furnace was higher than reached in the microwave oven for the formation of CNTs.

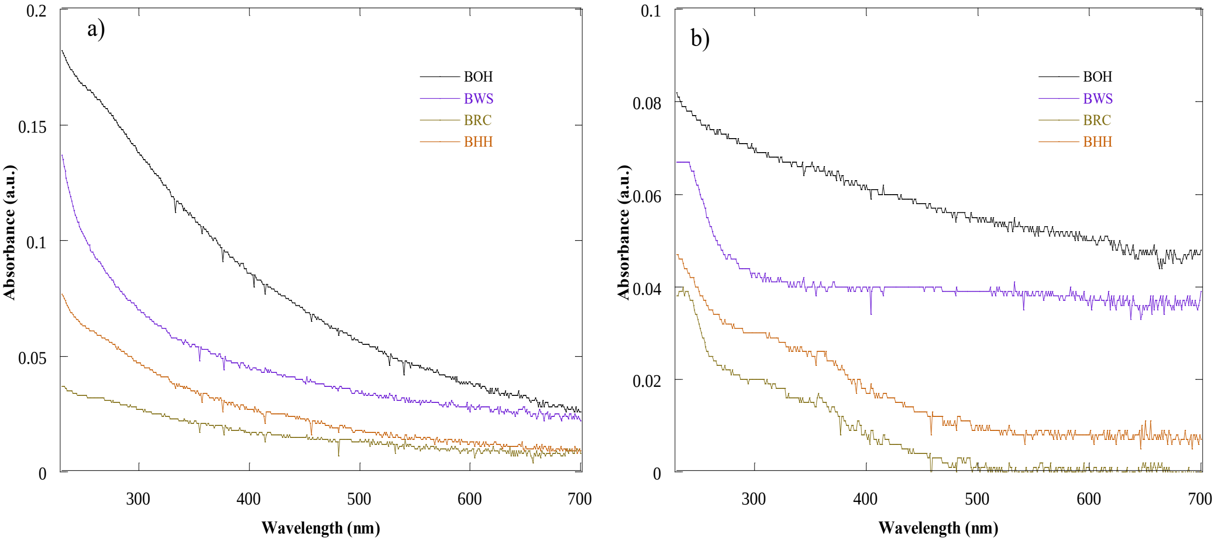

Figure 1. UV–vis absorbance spectra of CNTs suspensions in aqueous SDS synthesized from biochar a) Synthesis of CNTs into horizontal furnace b) Synthesis of CNTs into microwave oven. BOH: biochar of oat hull, BWS: biochar of wheat straw, BRC: biochar of rapeseed cake and BHH: biochar of hazelnut hull.

In Figure 2 the value of energy band gaps for synthesized CNTs through microwave irradiation and horizontal furnace, are shown. The *Eg* values of the synthesized CNTs were higher for synthesis using microwave irradiation, as shown in Figure 2.

Moreover, a characteristic of CNTs is that the energy band gap (*Eg*) is inversely proportional to the diameter [23]. According to the results, a high *Eg* value and lower hydrodynamic diameter was produced in the synthesis of CNTs at solvent self-ignition temperature in the horizontal furnace and using biochar of wheat straw. This effect can be attributed to the quantum confinement phenomenon, where an increase of the energy band gap and a decrease in particle size is produced [24].

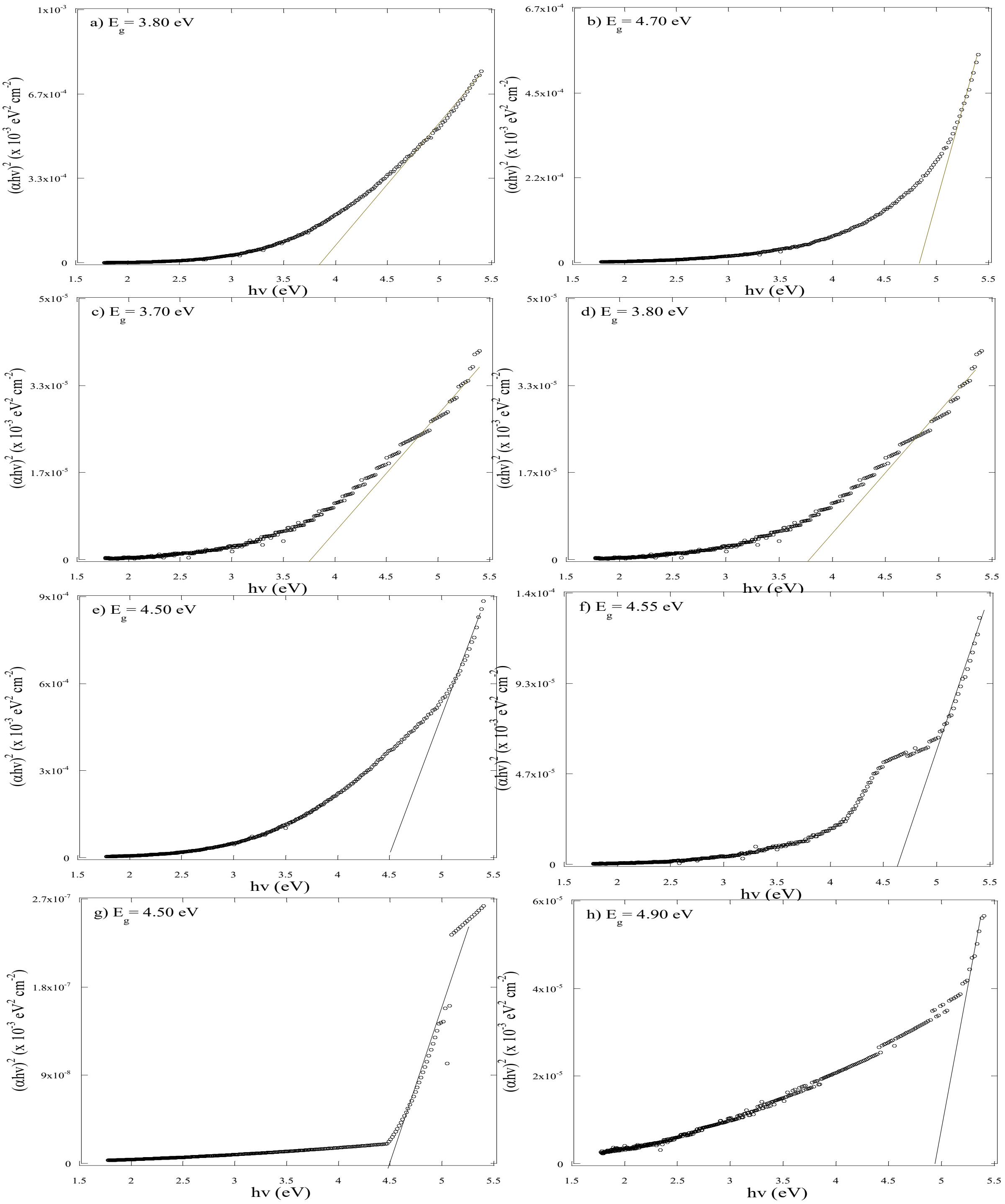

Figure 2. $(ahv)^2$ versus *hv* (eV, photon energy) plots of CNTs synthesized from a) BOH pyrolyzed in the horizontal furnace b) BWS pyrolyzed in the horizontal furnace c) BRC pyrolyzed in the horizontal furnace d) BHH pyrolyzed in the horizontal furnace e) BOH pyrolyzed in the microwave oven f) BWS pyrolyzed in the microwave oven g) BRC pyrolyzed in the microwave oven h) BHH pyrolyzed in the microwave oven

3.3. Degree of wall graphitization of crystal structure

The quality of CNTs samples has been estimated from the intensity ratio between D-band (I_D) and G-band (I_G)[25] of Raman spectra. In Table 3, the intensity ratio of the peaks is shown, I_G/I_D for CNTs growth by solvent self-ignition temperature in the horizontal furnace and using biochar. From Raman spectra, two main characteristic peaks appear, located around 1560 and 1300 cm^{-1}, corresponding to ordered carbon atom (G-band) and disordered carbon atoms (D-band), respectively[25]. The G-band and D-band are associated to CNTs [26, 27]. The D-band is usually attributed to the presence of amorphous or disordered carbon and the G-band is characteristic of graphitic structures in the CNTs [2, 27]. Intensity ratios I_G/I_D were higher for CTNs synthetized from oat hull biochar. The higher I_G/I_D ratio is indicative of a higher degree of wall graphitization, suggesting a better quality of the material using oat hull biochar [28]. With respect to the full width half maximum (FWHM$_G$) value of G-band, considering as a measure of the disorder level, a low FWHM values were obtained using biochar, indicating a small disorder structure level. We previously reported the use of biochar in the CNTs synthesis, under a method of microwave irradiation, where the values of both FWHMG and intensity ratio *I*G/*I*D in CNTs was an indicator of aromaticity of the precursor benefited by CNTs growth[4]

Table 3. Comparison of Raman I_G/I_D ratio and FWHM$_G$ for CNTs growth by solvent self-ignition temperature into horizontal furnace and using biochar. BOH: biochar of oat hull, BWS: biochar of wheat straw, BHH: biochar of hazelnut hull, BRC: biochar of rapeseed cake.

Biochar	I_G/I_D	FWHM$_G$
BOH	1.21	59.11
BWS	1.15	68.13
BHH	1.17	55.15
BRC	0.99	80.22

4. Conclusions

The use of biochar for CNT synthesis by the novel method of solvent self-ignition was developed. CNTs synthesized from biochar with the solvent presented higher CNT concentrations when they were developed in the horizontal furnace. This may be caused by the amount of energy release generated from the auto-ignition solvent in the furnace, which was higher than that reached in the microwave oven for the formation of CNTs. The synthesis of CNTs from biochar presents a sustainable lignocellulosic residual biomass management solution, adding value to agro-industrial biomass and an alternative option for biochar application in the construction industry. The results indicate that CNTs obtained by autoignition show a higher degree of wall graphitization, suggesting suitable CNT quality.

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