Synthesis of Carbon Nanotubes (CNT) by Chemical Vapor Deposition (CVD) using a biogas-based carbon precursor: A review

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Abstract. Carbon is the fourth most abundant element in the universe. Among all carbon allotropes, carbon nanotube (CNT) with a cylindrical tube structure becomes an attractive carbon nanomaterial due to its unique physical and chemical properties. The typical gas sources that are usually used in CNT synthesis are mostly hydrocarbons, e.g., alcohol, methanol, methane (CH₄), ethylene (C₂H₄), acetylene (C₂H₂), propane (C₃H₈), and cyclohexane (C₆H₁₂). Unfortunately, those carbon precursors are not environmentally friendly due to their origin from fossil fuels. Considering its continuity production, utilizing “green” alternatives and inexpensive materials will be more promising for industrial-scale production. Biogas is one of the alternative ideas as a carbon precursor in the process of CNT synthesis. Biogas consists of 40–60% methane (CH₄), 40–60% carbon dioxide (CO₂), and traces of nitrogen (N₂), oxygen (O₂), hydrogen sulfide (H₂S), hydrogen (H₂), and ammonia (NH₃). The most commonly used to produce CNT is CH₄ through chemical vapor deposition (CVD). CVD is the most expectant and scalable method for future power and electronic devices with its economical and straightforward friendly design.

1. Introduction
Carbon is one of the chemical elements that is the fourth most abundant element in the universe after oxygen. Carbon was found a long time ago in the form of charcoal or soot, then its admission as an element emerged in eighteenth later [1]. Allotropy or allotropes form if one element exists in two or more different structures, due to its different bonding way [2], resulting in a new form of materials with the same content. Diamond, graphite, carbone, fullerenes, nanotubes, graphene, and amorphous carbon are well-known as carbon allotropes, which have various unique structures with each remarkable properties [3]. Due to their remarkable properties, carbon allotropes have various applications such as catalyst supports, adsorbents, gas-storage, separation technology, battery electrodes, porous template materials, fuel cells, and biological cells. Carbon shows many outstanding chemical and mechanical properties, e.g., high melting and sublimation points, and easy to form diverse compounds due to its ability to form long carbon-to-carbon chains [4].

Carbon nanotube (CNT) is one of the most attractive nanomaterials among the other carbon allotropes, which has a cylindrical tube structure. CNT is a furled graphene sheet in which every layer consists of a hexagonal carbon ring arranged by sp² hybridized atom carbons [5]. CNT was discovered by Sumio Iijima, a scientist from Japan, in 1991. Firstly, it was made from the arc discharge method when synthesizing fullerenes. CNT seemed like extended fullerences with a diameter of around 0.7 nanometers and a length up to several micrometers [6, 7]. Iijima and other scientists found this material
as a remarkable substance. Many studies have been done to improve and develop CNT, creating CNT with high strength, stiffness, and electrical conductivity for amplifying the material composites and nano-electronic applications [8].

CNT is categorized into two types depending on the amount of graphite layer rolled up, i.e., single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) [9]. As is shown in Figure 1, SWCNT consists of one layer of graphite, similar to ordinary straw with a diameter of 1.4 nm or less. In comparison, MWCNT has more than one layer of graphite with a diameter of around 2–25 nanometers [10]. Carbon nanotubes have a type of sp² carbon hybridization [11]. SWCNT is classified in different structure forms, i.e., zigzag, armchair, and chiral structures. The chiral vector in CNT is marked with (n, m) indices. Integers n and m directions influence the number of unit vectors in graphene honeycomb crystal lattice. Zigzag structure means if m is zero; armchair structure means if the m = n; then chiral structure means the other state of zigzag and armchair. In addition, MWCNT has two structural models, namely the Russian doll model (smaller diameter) and the parchment model (a sheet of graphene rolled up around itself) [12].

![Figure 1. A bundle of (a) SWCNT and (b) MWCNT.](image)

In the CNTs synthesis, there are several parameters to determine the success of CNT growth, such as a catalyst, temperature of substrate, gas mixture, and gas pressure [13]. Carbon precursor gas decides a high impact on the growth of CNT. The typical gases used in CNT synthesis are mostly hydrocarbons, such as alcohol, methanol, methane (CH₄), ethylene (C₂H₄), acetylene (C₂H₂), propane (C₃H₈), and cyclohexane (C₆H₁₂). Unfortunately, most gas sources come from fossil fuels; thus, they have several disadvantages, such as their unrenewable material and the high cost [14]. Therefore, this review will discuss an alternative gas precursor in the synthesis of carbon nanotubes, i.e., biogas from waste material. The utilization of biogas can minimize the use of unrenewable gas as a carbon precursor in the synthesis of CNT.

2. Synthesis carbon nanotubes

CNT is one of the carbons allotropes, which has recently been developed. Because of its chemical, electrical, mechanical, and thermal properties [6], CNT are potentially transformed into many applications like biotechnology [15], nano-electronics [16], and thermal management. The synthesis methods to make CNT are also continuously developed and discovered.

Various methods are studied to gain CNT, such as arc discharge, chemical vapor deposition well-known as CVD [17], arc discharge, laser ablation [18], and electrolytic [19]. The main parameters in CNT synthesis are substrate temperature, gas pressure, gas mixture, and catalyst [20]. The arc discharge method can be applied by resulting energy from DC between graphitic anode and cathode with a chamber filled with helium gas. The arc occurred creates a high-temperature plasma (>4000 K), which sublimes the carbon precursors in the anode. The arc discharge method brings advantages, such as fast production of CNT with few defects; however, the method is not easy-controlled and has low productivity. Next, laser ablation is a method that prepares CNT at high temperature (±1200 °C) using
a laser, in which the process was generally conducted in an inert atmosphere. This method transforms carbon species to be graphitic materials with a metal catalyst, using a laser applied to vaporize the carbon. Laser ablation offers CNTs synthesized for higher purity than those generated by arc discharge, but less productivity of CNT. Among the various methods to synthesize CNTs, CVD is currently the most widely used due to its low cost, high productivity, scalability, and easy controllability [21].

Compared with other methods, chemical vapor deposition (CVD) is a low cost, high productivity, scalability, easy controllability, per chance, and scalable method for future power and electronic devices [22]. Impurities that come out from the synthesis of CNT affect the quality impact of CNT. However, sometimes the metal impurities give additive strength properties to CNT [23]. Liu et al. [24] reported that the most effective catalyst metals for carbon nanotube production using CVD are iron (Fe), nickel (Ni), and cobalt (Co) because of their high carbon solubility, excellent chemical and mechanical properties, and diffusion rate of carbon.

The CVD process typically uses a furnace chamber. Initially, all gases inside the chamber are removed to avoid the oxidation process which might be caused by oxygen-containing gases in the atmospheric air. The carbon precursor gases (particularly hydrocarbon) are then escorted into the reaction chamber together with an inert gas like helium or argon. The furnace is then heated to vaporize and decompose the gases resulting in the reaction between the reactive species coming from gases with catalyst, producing the deposition carbon on the substrate. Hydrogen as the residue gas will be exhausted from the chamber by the elimination system [25]. The schematic process of CVD is shown in Figure 2. The vapor decomposition occurs in the range of temperature 600-1200°C. The vapor hydrocarbons will interact with metal catalyst until they break down into hydrogen and carbon. Carbon will dissolve into the metal, while hydrogen will evaporate [26]. The economically-friendly and straightforward experimental setup becomes one reason to choose the CVD to be a method for synthesizing CNT. Many hydrocarbons can be used as precursors in various states of compounds, i.e., gas, liquid, or solid. As a result, it makes some possibilities to build many kinds of CNT growth, such as thick and thin films, coiled or straight nanotubes, powder, entangled or aligned, or desired architecture of nanotubes on a patterned substrate [6, 7].

![Figure 2: Schematic of the CVD process.](image)

Based on substrate-catalyst interaction, the CNT growth is classified into two types, tip-growth and base growth. Tip-growth means the catalyst presence above the CNT, while in base-growth, the catalyst presence at the base of CNT. Tip-growth is a weak substrate-catalyst interaction. CNT starts growing from the metal base and keeps growing up to have enough space to decompose hydrocarbons depending on the metal concentration gradient. At this mechanism, CNT keeps pushing apart the metal from the substrate. In contrast, in base growth, CNT is not strong enough to push metal because of the strong substrate-catalyst interaction, resulting in the growth mostly happens above the metal [24, 26].
3. Biogas from waste materials as carbon precursor of synthesis CNT

Successful CNT growth depends on the effective decomposition of the carbon precursor with the formation of stable catalysts that impact the arrangement of carbon lattice [27]. Common carbon precursors usually used are acetylene, xylene, benzene, toluene, and methane. However, those carbon precursors usually come from fossil fuels. The unrenovable resources have disadvantages for a sustainable environment, such as high cost and low availability. Considering its continuity production, utilizing a “green” carbon precursor will be an alternative way to synthesis CNT. The benefit of using natural precursors is having less cost, long-term material, pathogen reduction, and saving energy consumption [28]. One of the alternative carbon precursors to synthesis CNT is biogas.

Biogas is a mixture gas that has components about 40%–60% methane (CH₄), 40%–60% carbon dioxide (CO₂), along with traces of oxygen (O₂), hydrogen (H₂), nitrogen (N₂), hydrogen sulfide (H₂S), then ammonia (NH₃) [29]. Biogas is the result of anaerobic digestion or fermentation, which exploits kinds of waste like animal manure [30], agricultural waste [31], and organic waste [32]. Waste generation increases every year, coming from agricultural production and household consumption. Around the world, it represents about 1.3 billion tons of waste per year [33].

The source of biogas can be obtained from cattle dung, animal manure, food waste or digested slurr, straw, human and animal feces, leaves, weeds, leaf, poultry waste, domestic rubbish, and industrial wastes [28, 34]. Indonesia, as a country with a big population, carries out a high strength to implement from waste to energy, including the generation of biogas by anaerobic digestion. Many studies have reported specific types of utilization waste materials as potential economic sources in bioconversion for making biogas [35].

Cattle manure or cattle dung is categorized as biomass, which means alternative source energy from living materials such as plants and animals. There are few ways to convert biomass into energy by burning material (woody things or grasses): decomposing biomass with various conditions like temperature, pressure, and catalyst to acquire combustible yield, or applying an anaerobic digestion process in which microorganisms split up biomass without oxygen to produce biogas (particularly CO₂ and CH₄) [36]. Biomass can be sustainable and renewable feedstock that comprises carbon-rich material, chemicals, and biofuels [37].

Biomass can be converted into biogas by four steps, as shown in Figure 3. They consist of hydrolysis, acidogenesis, acetogenesis, and methanogenesis, resulting in methane gas. In the first stage of hydrolysis, this process makes a complex proteins, carbohydrates, and fats which were contained in waste, into monomers by bacterial cellulose and exoenzymes. Following the first stage, in the second step of acidogenesis, the degradation continually proceeds into short-chain acid. Then, for acetogenesis, that short-chain will be converted to be CH₃COOH, CO₂, and H₂. The last step is methanogenesis, which the intermediates are transformed into CO₂ and methane [38]. Biogas technology works as a complete system to put forward the conversion energy, factors of waste material, and environmental and renewable sources [39]. Other factors that make the bioconversion of organic waste successfully produce biogas are temperature, environmental conditions, pH, retention time, organic mixture material, and reactor configuration [33].

![Figure 3. Schematic process of conversion waste material into biogas.](image-url)
Budiyono et al. studied making biogas from solid waste (cattle manure) and liquid waste (rumen fluid) [40]. Solid waste is filtered from the slurry form but keeping it full of bacteria. All the waste collected needed to be homogenized. Both of various wastes are heated to 105 and 600 °C. The biodigester system used a batch system. The biodigester chambers were created from polyethylene bottle plugs, then connected with biogas measurement. The heater temperature of the biodigester was controlled by a water bath. As a result, the biogas formed was measured by the liquid displacement method. Rumen fluid made a positive impact on increasing the production rate of biogas. Rumen fluids gave influence into cumulative biogas production and kinetic rate of biogas production. The optimum temperature for bacteria was at 38.5 °C to degrade the organic substrate. By the adding of rumen fluid inoculums, the process produced more biogas (A: 194.4 (ml/gVS); meanwhile, the process without adding rumen fluids resulted in lower yield (A: 58.16 ml/gVS).

Godi et al. had other experiments in making bio-digester, which consisted of a digestion chamber, slurry inlet and outlet, gas exit, cap, and scrambler [41]. The methane gas was not only the gas resulted; the other gas (carbon (IV) oxide and hydrogen sulfide) was also detached from the digestion process chamber. Consequently, it required something that can get rid of those gases. In their experiment, Ca(OH)₂ was used as a gas remover for undesired gases. The steps of making the biodigester were initially by the cow dung. First, waste prepared from cow dung was blended with water in the chamber to make a slurry. The mixture was moved down into the digester through the inlet. Second, they made a pipe connection between the gas source pipe and the digester chamber and also with the collecting container. The pipe also was passed by the solution of prepared calcium hydroxide to remove another gas. Next, another outlet pipe was linked up with the conical flask. By giving candle wax on the connected pipe, the gas leak was reduced. The calibrated drum was let to have fermentation; then, the produced gas was collected through the upward delivery method. The process took time for almost 20 days for fermentation from cow dung into biogas because cow feed mainly contains fibrous substances so that it took longer to decay by microorganisms. As a result, the total methane yielded is 1570 ml, and the total biogas yield is 2300 ml. Therefore, the production of methane compounds is 68% of the total composition of biogas generated from cow dung.

4. Synthesis of carbon nanotubes using biogas-based carbon precursor

Biogas converted from waste material is potentially used as the carbon precursor in the synthesis of CNT, especially for the methane gas produced from biogas bioconversion of waste. Khavarian and Mohammed [42] studied the biogas reforming over MWCNT. They used a nanocomposite catalyst such as Co-Mo/MgO catalyst and methane (CH₄) gas in CVD. The CVD process was conducted in a continuous rotary reactor at temperature 825 °C and was supplied with N₂ as a carrier gas. The average diameter of the MWCNT ranges between 10 and 30 nanometers. The increasing of the CO₂/CH₄ feed ratio influenced higher methane conversion and a lower H₂/CO syngas ratio as CO formation reactions.

Baddour et al. [43] also explained the process of synthesis CNT using the CVD furnace. The CVD system is composed of a quartz tube, gas inlet, thermocouple, and pump. The quartz tube was placed in the furnace. Then, the substrates are located inside the quartz tube in the middle of the furnace cap. In this experiment, acetylene (C₂H₂) was used as a carbon precursor and nitrogen (N₂) as the carrier gas, which entered the quartz tube from the gas inlet. The furnace system temperature was set at a temperature of 650, 700, and 800 °C with substrate pre-heating at 850°C for 30 minutes and at 650, 700, 800, and 850°C without pre-heating. The nanotubes resulting in are kind of MWNT with a range of diameter around 20 to 70 nanometers.

In another study, Vamathevan developed the process of synthesizing carbon nanotubes from biogas [44]. The study made the chamber consisted of argon and biogas cylinders that were connected to the reactor. The sample of catalyst material was kept in the sample holder. After the holder was inserted to the gas cylinder, the synthesis of carbon nanotubes using biogas is ready to run. The reactor was heated up to 550°C when the biogas was delivered into the reactor for one hour. In the end, after an hour of gas supply, the reactor got cooled down to room temperature. The product of the reaction was then taken out and was characterized. This work successfully developed a process to synthesize carbon nanotubes.
using biogas and the catalysts of nickel particles deposited on the support surface. However, the results of a product characterization suggested that the synthesis process of the CNT produced using biogas needs to be more developed by optimizing the synthesis parameters.

5. Conclusion
Carbon precursor gas takes a high impact on the growth of CNT. The commonly used hydrocarbon gases have several disadvantages, such as limited availability, unrenewable, and high cost. The synthesis of CNT can be conducted by CVD method, which is the most profitable method to synthesis CNT that brings many conveniences. Utilization of biogas converted from waste material as a carbon precursor of synthesis CNT confidently provides an alternative sustainable gas resource. The biogas can be produced from anaerobic digestion or fermentation, which exploits kinds of waste like animal manure, agricultural waste, and organic waste. The biogases produced can be used as alternative gas to synthesis CNT as the carbon precursor via CVD method.

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References
[1] Weeks M E 2018 Discovery of The Element (Sagwan Press)
[2] McNaught A D and Wilkinson A 1997 Compendium of chemical terminology vol 1669 (Blackwell Science Oxford)
[3] Falcao E H and Wudl F 2007 J. Chem. Technol. Biotechnol. 82 524
[4] Rahman T, Fadhlulloh M A, Nandiyanto A B D and Mudžakir A 2015 Jurnal Integrasi Proses 5 120-31
[5] Holban A M, Grumezescu A M and Andronescu E 2016 Surface Chemistry of Nanobiomaterials, ed A M Grumezescu (William Andrew Publishing) pp 301–327
[6] Sengupta J 2018 Handbook of Nanomaterials for Industrial Applications ed C Mustansar Hussain (Elsevier) pp 172–194
[7] Meyyappan M, Delzeit L, Cassell A and Hash D 2003 Plasma Sources Sci. Technol. 12 205
[8] Öncel Ç and Yürüm Y 2006 Fuller. Nanotub. Car. N. 14 17
[9] Shashikumar N S, Gireesha B J, Mahanthesh B and Prasannakumara B C 2018 Multidiscip. Model. Mater. Struct. 14 769
[10] Caglar B 2010 Production of carbon nanotubes by PECVD and their applications to supercapacitors Master’s Thesis (Universitat de Barcelona)
[11] Manawi Y M, Samara A, Al-Ansari T and Atieh M A 2018 Materials 11 822
[12] Eatmadi A, Daraea H, Karimkhlanloo H, Kouhi M, Zarghami N, Akbarzadeh A, Abasi M, Hanifehpour Y and Joo S W 2014 Nanoscale Res. Lett. 9 393
[13] Barnard J S, Paukner C and Koziol K K 2016 Nanoscale 8 17262
[14] Alfarisa S, Abu Bakar S, Mohamed A, Hashim N, Kamari A, Md Isa I, Mamat M H, Rahman Mohamed A and Rusop Mahmood M 2015 Adv. Mat. Res. 1109 50
[15] Saito Y, Hamaguchi K, Hata K, Uchida K, Tasaka Y, Ikazaki F, Yamura M, Kasuya A and Nishina Y 1997 Nature 389 554
[16] Martin C R and Kohli P 2003 Nat. Rev. Drug Discov. 2 29
[17] Gattia D M, Vittori Antisari M, Marazzi R, Pilloni L, Contini V and Montone A 2006 Mater. Sci. Forum 518 23
[18] Batani D, Vinci T and Bleiner D 2014 Laser Part. Beams 32 1
[19] Novoselova I A, Oliynyk N F, Volkov S V, Konchits A A, Yanchuk I B, Yefanov V S, Kolesnik S P and Karpets M V 2008 Physica E Low Dimens. Syst. Nanostruct. 40 2231
[20] Gohier A, Minea T M, Point S, Mevellec J Y, Jimenez J, Djouadi M A and Granier A 2009 *Diam. Relat. Mater.* **18** 61
[21] Kwon S-J, Seo H-K, Ahn S and Lee T-W 2019 *Adv. Sustain. Syst.* **3** 1800016
[22] Quinton B T, Barnes P N, Varanasi C V, Burke J, Tsao B-H, Yost K J and Mukhopadhyay S M 2013 *J. Nanomater.* **2013** 356259
[23] Williams P T 2020 *Waste and Biomass Valorization* (Springer)
[24] Liu X, Shen B, Wu Z, Parlett C M A, Han Z, George A, Yuan P, Patel D and Wu C 2018 *Chem. Eng. Sci.* **192** 882-
[25] Kumar M and Ando Y 2010 *J. Nanosci. Nanotechnol.* **10** 3739
[26] Venkataraman A, Amadi E V, Chen Y and Papadopoulos C 2019 *Nanoscale Res. Lett.* **14** 220
[27] Nessim G D, Seita M, Plata D L, O’Brien K P, John Hart A, Meshot E R, Reddy C M, Gschwend P M and Thompson C V 2011 *Carbon* **49** 804
[28] Kumar R, Singh R K and Singh D P 2016 *Renew. Sustain. Energ. Rev.* **58** 976
[29] Köhring M, Böttger S, Willer U and Schade W 2015 *Sensors* **15**
[30] Bidart C, Fröhling M and Schultmann F 2014 *Renew. Sustain. Energ. Rev.* **38** 537
[31] Karellas S, Boukis I and Kontopoulos G 2010 *Renew. Sustain. Energ. Rev.* **14** 1273
[32] Zhang C, Su H, Baeyens J and Tan T 2014 *Renew. Sustain. Energ. Rev.* **38** 383
[33] Khanal S K, Nindhia T G T and Nitayavardhana S 2019 *Sustainable Resource Recovery and Zero Waste Approaches* (Elsevier) pp 165–74
[34] Adeniran K A, Ahaneku I E, Itodo I N and Rohjy H A 2014 *Agric. Eng. Int.: CIGR Journal* **16** 126
[35] Khalil M, Berawi M A, Heryanto R and Rizalie A 2019 *Renew. Sustain. Energ. Rev.* **105** 323
[36] Hoa L Q, Vestergaard M d C and Tamiya E 2017 *Sensors* **17**
[37] Wang Z, Shen D, Wu C and Gu S 2018 *Green Chem.* **20** 5031
[38] Faisal S, Yusuf Hafeez F, Zafar Y, Majeed S, Leng X, Zhao S, Saif I, Malik K and Li X J A S 2019 *Appl. Sci.* **9** 59
[39] Arvanitoyannis I S and Tserkezou P 2008 *Int. J. Food Sci. Technol.* **43** 958
[40] Budiyono I, Nyoman I, Widiasa, Sunarso S and Seno J 2010 *Int. J. Chem. Biol. Eng.* **3** 39
[41] Godi N Y, Zhengwuvi L B, Adulkadir S and Kamtu P M 2013 *J. Mech. Eng. Res.* **5** 1
[42] Khavarian M, Mohamed A R, Ibrahim S M and Noorsal K 2017 *AIP Conference Proceedings* **1901** 030008
[43] Baddour C E, Fadlallah F, Nasuhooglu D, Mitra R, Vandsburger L and Meunier J-L 2009 *Carbon* **47** 313
[44] Vamathevan K 2011 *The Development of the Process to Synthesize Carbon Nanotubes from Biogas* Master's Thesis (University of Moratuwa)