

PRODUCTION OF SMALL DIAMETER CARBON NANOTUBES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of Singapore application No. 10202101648Q, filed on 18 February 2021, the contents of it being hereby incorporated by reference in its entirety for all purposes.

FIELD OF THE INVENTION

[0002] This disclosure relates to the field of chemistry and synthesis. In particular, the present invention relates to method and apparatus for production of small diameter carbon nanotubes (CNTs).

BACKGROUND OF THE INVENTION

[0003] Carbon nanotubes (CNTs) find use in many applications, such as, but not limited to electronics, energy storage devices, polymer composites, automotive, and aerospace manufacturing. Chemical vapor deposition (CVD) method is the main method currently employed for the synthesis of CNTs. CVD is typically carried out using transition metal catalysts (e.g., Fe, Ni, Co, Mo and their mixtures) and non-condensable hydrocarbon gases (e.g., methane, acetylene) or carbon monoxide.

[0004] Generally, high selectivity towards small diameter CNTs is currently being achieved by using simple precursor gases. For instance, the composition of gas for the growth of single-walled or small diameter (such as few-walled) CNTs could consist of one hydrocarbon compound (precursor) and inert gas (for instance, precursors can be CH₄, hexane, cyclohexane, benzene, naphthalene and anthracene mixed with argon as a carrier gas (Li et al., 2004)) or hydrocarbon and hydrogen gas (methane and hydrogen (Tang et al., 2001; Flahaut et. al., 2005)). The individual hydrocarbon compounds and hydrogen must be produced through purification and separation of natural gas and/or gases from petrochemical plants, for instance, using pressure swing adsorption. The individual gas components must then be mixed again resulting in an expensive and unwieldy process to synthesize small diameter CNTs which are predominantly below about 10 nm in diameter.

[0005] Furthermore, the literature currently shows compositions of gases containing mixtures of various hydrocarbons produces mixtures of multi-walled CNTs that have large content of nanotubes with outer diameters above 10 nm. Veksha et al. (2017) reported the synthesis of CNTs from mixtures of various hydrocarbons produced by pyrolysis of low-density polyethylene (LDPE), polypropylene (PP) and a mixture of plastics containing 40 wt.% LDPE, 40 wt.% PP, 10 wt.% polystyrene and 10 wt.% polyethylene terephthalate. The obtained mixtures of multi-walled CNTs contained more than 80-86% CNTs with outer diameters above 10 nm. Aboul-Enein and Awadallah (2019) synthesized mixtures of multi-walled CNTs containing more than 72-90% CNTs with outer diameters above 10 nm using hydrocarbon gas mixtures obtained by LDPE pyrolysis. Aboul-Enein (2018) reported mixtures of multi-walled CNTs containing more than around 48% CNTs with outer diameters above 10 nm from PP. Gou et al. (2020) synthesized multi-walled CNTs with diameters 15-20 nm using mixtures of hydrocarbons produced by thermal decomposition of phenolic formaldehyde resin. Wu et al. (2016) utilized mixtures of hydrocarbons obtained by pyrolysis of waste PP to synthesize multi-walled CNTs with outer diameters around 30 nm. Yao et al. (2017) utilized a mixture of hydrocarbons produced by pyrolysis of waste plastics and obtained multi-walled CNTs with outer diameters between 20 nm to 50 nm depending on the catalyst. Yang et al. (2017) reported the synthesis of multi-walled CNTs with outer diameters above 12 nm using mixtures of hydrocarbons produced by pyrolysis of a mixture of PP and polyethylene (PE). Jia et al. (2020) synthesized multi-walled CNTs with mean outer diameters between 27 nm to 93 nm using gases containing various hydrocarbons produced by pyrolysis of PP and PE.

[0006] One of the major challenges therefore is how to convert hydrocarbon gas mixtures containing multiple hydrocarbon compounds into mixtures of CNTs that contain large fraction of small diameter CNTs (i.e., CNTs with outer diameters below about 10 nm) in a simple and effective way.

[0007] Thus, there is a need for a method or an apparatus or a system capable of producing small diameter CNTs using hydrocarbon gas mixtures containing multiple hydrocarbon components (without the separation, purification and mixing of the individual gas components described above).

SUMMARY OF THE INVENTION

[0008] In one aspect, there is provided a method of producing small diameter CNTs from a feed gas obtained by heating a polyolefin-containing feedstock, comprising the steps of:

- (a) flowing the feed gas into a first reaction zone containing a first catalyst, wherein a portion of the feed gas is partially decomposed into an intermediate gas and solid carbon; and
- (b) flowing the intermediate gas into a second reaction zone containing a second catalyst, wherein a portion of the intermediate gas is converted into small diameter CNTs.

[0009] In another aspect, there is provided a small diameter CNT produced by the method above.

[0010] In another aspect, there is provided an apparatus for production of small diameter CNTs, the apparatus comprising:

a first reactor which is connected to a second reactor in series; wherein the first reactor is configured to hold a first heated catalyst bed comprising a first catalyst, wherein the first catalyst bed generates an intermediate gas and solid carbon when the first catalyst bed is in contact with a feed gas received from an inlet; and the second is reactor configured to hold a second heated catalyst bed comprising a second catalyst, wherein the second catalyst bed generates the small diameter CNTs when the second catalyst bed is in contact with the intermediate gas received from the first reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The invention of the present disclosure will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

[0012] FIG. 1 shows a system for production of small diameter CNTs comprising a series of two reactors with the first reactor (Reactor 1) used for partial decomposition of feed gas and the second reactor (Reactor 2) used for the production of small diameter CNTs: (1) generation of feed gas from plastics, (2) gas pump, (3) pressurized gas storage vessel, (4) flow controlling device, (5) source of diluent gas (examples of diluent gases are, but not limited to, inert gases

such as nitrogen or argon; other examples of diluent gases are hydrogen and methane), (6) pressure regulator, (7) pressure measurement device, (8) heater and Reactor 1 with the first catalyst for partial decomposition of feed gas, (9) particle filtration device, (10) heater and Reactor 2 which contains the second catalyst for small diameter CNT production.

[0013] FIG. 2A shows a FESEM image of multi-walled CNTs produced in Reactor 1 and FIG. 2B shows the outer diameter distribution of multi-walled CNTs from Reactor 1 (total number of CNTs = 160).

[0014] FIG. 3A shows bundles of small diameter CNTs produced in Reactor 2 from intermediate gas (bar = 50 nm). FIG. 3B and FIG. 3C show the morphology of CNTs at low magnification from two different areas (bars = 5 nm). FIG. 3D shows the outer diameter distribution of CNTs (total number of CNTs = 175). FIG. 3E and FIG. 3F show corresponding large magnification images of the boxed areas marked in FIG. 3B and FIG. 2C, respectively.

[0015] FIG. 4A shows Raman spectroscopy of small diameter CNTs. FIG. 4B shows temperature programmed oxidation profiles of small diameter CNTs.

[0016] FIG. 5A shows composition of hydrocarbon compounds of diluted feed gas and intermediate gas before and after synthesis in Reactor 2 (balance N₂). FIG. 5B shows concentration of hydrogen, carbon monoxide and carbon dioxide of diluted feed gas and intermediate gas before and after synthesis in Reactor 2 (balance N₂).

[0017] FIG. 6A and FIG. 6B show carbon product obtained in Reactor 2 from diluted feed gas. FIG. 6C and FIG. 6D show corresponding large magnification images of the boxed areas marked in FIG. 6A and FIG. 6B, respectively.

[0018] FIG. 7 shows spherical carbon particles (unwashed) produced by thermal non-catalytic cracking of feed gas in Reactor 2 at 1000 °C.

[0019] FIG. 8A shows influence of initial V_f/n values on the content of paraffins in intermediate gas using two catalysts (40Co-10Mo and 26Fe-14Ni-10Mo). FIG. 8B shows influence of initial V_f/n values on the content of olefins in intermediate gas using two catalysts (40Co-10Mo and 26Fe-14Ni-10Mo).

[0020] FIG. 9A shows the values of V_f/n over time using the 40Co-10Mo catalyst. FIG. 9B shows concentrations of paraffins in the intermediate gas corresponding to the values of V_f/n over time using the 40Co-10Mo catalyst. FIG. 9C shows concentrations of olefins in the

intermediate gas corresponding to the values of V_f/n over time using the 40Co-10Mo catalyst. (Legends for FIG. 9A, 9B and 9C: Run 1 = Closed circles with solid line; Run 2 = Open circles with dashed line; Run 3 = Closed triangles with solid line; Run 4 = Open squares with dashed line; Run 5 = Open diamonds with dashed line; and Run 6 = Closed squares with dotted line.)

[0021] FIG. 10 shows carbon growth in a series of two reactors. Conditions: Reactor 1 (700 °C) and Reactor 2 (700 °C), feed gas from LPET and HPET feedstock, catalyst: 0.9 wt.% Ni supported on CaCO_3 .

[0022] FIG. 11 shows size distribution of CNTs grown in the series of two reactors. Conditions: Reactor 1 (700 °C) and Reactor 2 (700 °C), feed gas from LPET and HPET feedstock, catalyst: 0.9 wt.% Ni supported on CaCO_3 . The duration for the CVD reaction from top to bottom are 10 minutes (LPET), 20 minutes (LPET), 30 minutes (LPET) and 20 minutes (HPET).

[0023] FIG. 12A shows the representative images of multi-walled CNTs produced in Reactor 1 (700 °C) from feed gas from LPET feedstock (catalyst: 0.9 wt.% Ni supported on CaCO_3). FIG. 12B shows the representative images of multi-walled CNTs produced in Reactor 2 (700 °C) from feed gas from LPET feedstock (catalyst: 0.9 wt.% Ni supported on CaCO_3).

DEFINITIONS OF TERMS

[0024] The term “small diameter carbon nanotube” refers to any CNT with outer diameter below about 10 nm. The term “a mixture of small diameter carbon nanotubes” or “mixtures of small diameter carbon nanotubes” refer to any mixture of small diameter CNTs containing at least about 60% of CNTs with different outer diameters which are below about 10 nm.

[0025] The term “reaction zone” refers to a reactor vessel. The reactor vessel can be a catalytic reactor vessel. A reaction zone can also refer to a reactor, such as but not limited to, a catalytic reactor.

[0026] The terms “first reactor” and “Reactor 1” may be used interchangeably. The terms “second reactor” and “Reactor 2” may be used interchangeably.

[0027] The term “apparatus” may also refer to a system comprising combinations made of, but not limited to, two or more modules, components, reaction chambers, reactors, and vessels.

[0028] The term “initial flow rate” refers to the volumetric flow rate (L/min) within about the first 5 minutes of reaction.

[0029] The term “intermediate gas” refers to the gas at the outlet of the first reaction zone. This is the gas which remains after a portion of the feed gas is partially decomposed.

[0030] The term “partial” refers to incomplete or less than 100%.

[0031] The term “in series” refers to a configuration of an apparatus where the gas stream from a first reactor is further provided into a second reactor. It should be understood by a person skilled in the art that one or more devices or components may be further present in between the first reactor and the second reactor. The devices or components are for example, but not limited to, filtration devices, pressure regulators, storage vessels, gas boosters and flow controlling devices.

[0032] The term “diluent gas” refers to a gas that is used to decrease the concentration of hydrocarbons in the feed gas. Examples of diluent gases are, but not limited to, inert gases such as nitrogen or argon; other examples of diluent gases are hydrogen and methane. A diluent gas can comprise either one type of gas or a mixture of several gaseous compounds.

[0033] The term “carbonaceous” means consisting of or containing carbon or its compounds. Examples of carbonaceous materials are, but not limited to, wood, grass, plastics, textile and food.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0034] The upcycling of wastes (such as, but not limited to plastics, biomass and other carbonaceous materials) into higher value products such as carbon nanomaterials to manage waste – which would otherwise end up in landfills, has made some advances in terms of research. In particular, some researchers are attempting to produce carbon nanotubes (CNTs) from plastic waste. Polyolefins such as polyethylene (PE) and polypropylene (PP) are abundant components of plastic waste. However, chemical recycling of plastics containing polyethylene and polypropylene via pyrolysis followed by chemical vapor deposition typically results in the growth of mixtures of multi-walled CNTs with large content of CNTs having outer diameters between 10 nm to 100 nm. For instance, pyrolysis-derived hydrocarbon gas mixtures from plastics containing C1-C5 hydrocarbon compounds, CO, CO₂ and hydrogen were shown to yield mixtures of multi-walled CNTs that contain less than 52% CNTs with outer diameters below 10 nm when such gases were subjected to a catalyst in a CVD reactor (based on Veksha et al., 2017; Aboul-Enein and Awadallah, 2019; Aboul-Enein and Awadallah, 2018; Aboul-Enein et al., 2018; Gou et al., 2020; Wu et al., 2016; Yao et al., 2017; Yang et al., 2017; Jia et

al., 2020). One of the major challenges therefore is how to convert hydrocarbon gas mixtures containing multiple hydrocarbon compounds into mixtures of CNTs that contain large fraction of small diameter CNTs (i.e. CNTs with outer diameters below 10 nm) in a simple and effective way.

[0035] The present disclosure thus provides a method and an apparatus (or system) as described herein for the conversion of hydrocarbon gas mixtures containing multiple hydrocarbon compounds into small diameter CNTs in a simple and effective way. The present disclosure also provides small diameter CNTs produced from the method and apparatus as described herein. The small diameter CNTs produced by the method as disclosed herein avoids fossil resource consumption in the production of CNTs while reducing waste pollution. A valuable by-product of the method as disclosed herein is hydrogen which itself is a growing industry as the world economy moves towards a circular carbon neutral mode.

[0036] In one aspect, there is provided a method of producing small diameter CNTs from a feed gas obtained by heating a polyolefin-containing feedstock, comprising the steps of:

- (c) flowing the feed gas into a first reaction zone containing a first catalyst, wherein a portion of the feed gas is partially decomposed into an intermediate gas and solid carbon; and
- (d) flowing the intermediate gas into a second reaction zone containing a second catalyst, wherein a portion of the intermediate gas is converted into small diameter CNTs.

[0037] In one aspect, there is provided a method of producing small diameter CNTs from a feed gas obtained by heating a polyolefin-containing feedstock, comprising the steps of:

- (e) flowing the feed gas into a first reaction zone containing a first catalyst, wherein a portion of the feed gas is partially decomposed into an intermediate gas and solid carbon; and
- (f) flowing the intermediate gas into a second reaction zone containing a second catalyst, wherein a portion of the intermediate gas is converted into small diameter CNTs, wherein the small diameter CNTs are produced.

[0038] In another aspect, there is provided an apparatus (or system) for production of small diameter CNTs, the apparatus comprising:

- a first reactor which is connected to a second reactor in series; wherein

the first reactor is configured to hold a first heated catalyst bed comprising a first catalyst, wherein the first catalyst bed generates an intermediate gas and solid carbon when the first catalyst bed is in contact with a feed gas received from an inlet; and the second reactor is configured to hold a second heated catalyst bed comprising a second catalyst, wherein the second catalyst bed generates the small diameter CNTs when the second catalyst bed is in contact with the intermediate gas received from the first reactor.

[0039] In one example, the polyolefin-containing feedstock comprises one or more polyolefins selected from the group consisting of polyethylene, polypropylene, polymethylpentene, polybutene-1, ethylene-octene copolymers, olefin block copolymers, propylene-butane copolymers, polyisobutylene, poly(α -olefin)s, ethylene propylene rubber, ethylene propylene diene monomer rubber, or combinations thereof. In one example, the combination of polyolefins is a mixture of polyethylene and polypropylene.

[0040] Without being bound by theory, it is believed that the method and/or apparatus of the present disclosure may use any polyolefin-containing feedstock obtained from carbonaceous materials such as, but not limited to, wood, sawdust, agricultural residues, food residues, textile and plastics, to produce the feed gas. In another example, the polyolefin-containing feedstock can be a single type of carbonaceous materials or a mixture of different types of carbonaceous materials such as but not limited to, polyethylene and a mixture of polyethylene and propylene. In one example, the polyolefin-containing feedstock is plastic waste.

[0041] In one example, before the method of the disclosure is performed, the feed gas may be produced by heating of carbonaceous feedstock (for example, but not limited to, using a pyrolysis and/or cracking steps), followed by condensation of liquid hydrocarbon products (denoted as "oil") as shown in FIG. 1. The collected feed gas is a mixture of all gaseous components remaining in the gas phase after oil condensation. In another example, the feed gas can be either provided by pyrolyzing and condensing liquid products or by supplying from a storage of feed gas mixture obtained from a previous pyrolysis and oil condensation process.

[0042] In one example, the feed gas comprises a mixture of paraffins and olefins. In one example, the intermediate gas comprises a mixture of paraffins and olefins.

[0043] In one example, the feed gas comprises at least one or more paraffins. In one example, the feed gas comprises at least one or more olefins.

[0044] In one example, the intermediate gas comprises at least one or more paraffins. In one example, the intermediate gas comprises at least one or more olefins.

[0045] In one example, the feed gas and the intermediate gas comprise at least one or more paraffins. In one example, the feed gas and the intermediate gas comprise at least one or more olefins. In one example of the present disclosure, the feed gas and the intermediate gas comprise at least one or more paraffins and one or more olefins.

[0046] The method of the invention may be performed with cumulative content of paraffins in the feed gas of between about 10 vol.% to about 20 vol.%, between about 15 vol.% to about 25 vol.%, between about 20 vol.% to about 30 vol.%, between about 25 vol.% to about 35%, or between about 30 vol.% to about 40 vol.%. The method of the invention may be performed with cumulative content of olefins in the feed gas of between about 10 vol.% to about 20 vol.%, between about 15 vol.% to about 25 vol.%, between about 20 vol.% to about 30 vol.%, between about 25 vol.% to about 35%, or between about 30 vol.% to about 40 vol.%, or between about 35 vol.% to about 45 vol.%, or between about 40 vol.% to about 50 vol.%, or between about 45 vol.% to about 55 vol.%. In one example, the cumulative content of paraffins in the feed gas is between about 11.5 vol.% to about 13.0 vol.%. In one example, the cumulative content of olefins in the feed gas is between about 38.4 vol.% to about 41.4 vol.%. In one example, the cumulative content of paraffins is between about 11.5 vol.% to about 13.0 vol.%, and the cumulative content of olefins is between about 38.4 vol.% to about 41.4 vol.% in the feed gas.

[0047] In one example, the content of olefins in the feed gas is higher than that of paraffins. The method of the invention may be performed with paraffins/olefins ratio in the feed gas of between about 0.1 to about 0.25, between about 0.2 to about 0.35, between about 0.3 to about 0.45, between about 0.40 to about 0.55, between about 0.5 to about 0.65, between about 0.6 to about 0.75, or between about 0.7 to about 0.99. In one example, the paraffins/olefins ratio in the feed gas is between about 0.30 to about 0.31.

[0048] In one example, the feed gas contains a mixture of paraffins and olefins with C1-C5 carbon atoms, and may optionally further comprise H₂, CO, CO₂ and N₂. In one example, the composition of feed gas utilized for the synthesis of CNTs is as summarized in Table 1.

[0049] In one example, the feed gas is mixed with a second gas component (also referred to in the present disclosure as “diluent gas”). In one example, the diluent gas can be added to the feed gas to decrease the concentration of hydrocarbons to a suitable concentration as feed gases may vary in hydrocarbon concentrations between batches. The invention described herein may be performed using diluent gas comprising one or more types of inert gases. The term “diluent gas mixture” refers to a mixture of one or more types of diluent gases. Examples of diluent gases are, but not limited to, inert gases such as nitrogen or argon. Other examples of diluent

gases are, but not limited to, hydrogen and methane. The diluent gas can be mixtures of several compounds. In one example, the diluent gas (or diluent gas mixture) comprises a mixture comprising, but not limited to, an inert gas, gaseous hydrocarbons and hydrogen. Without being bound by theory, it is believed that the method and/or apparatus of the present disclosure may use any gas (or gas mixtures) that is not chemically reactive or a gas (or gas mixtures) which decomposes at a slow or negligible rate under the conditions performed by the method or apparatus of the present disclosure, such as, but not limited to, nitrogen or argon.

[0050] In one example, the diluent gas (or diluent gas mixtures) can be supplied to the pyrolysis equipment (which is used prior to the method or apparatus of the present invention) and used as a carrier to remove volatile pyrolysis products from the reactor. Thus, in another example, the feed gas can also contain diluent gas (or diluent gas mixtures) from a compressed gas cylinder. Without being bound by theory, it is believed that the method and/or apparatus of the present disclosure may use feed gas which is provided continuously, semi-continuously or in batches. In one example, the feed gas is preferably provided continuously into the first reaction zone which minimizes fluctuations of gas concentrations supplied to the first reaction zone.

[0051] In one example of the apparatus described herein, the inlet of the first reactor is connected to a pressurized gas storage vessel holding the feed gas, wherein the feed gas flow rate is controlled by a flow controlling device so that a specific initial ratio between volumetric flow rate (L/min) and molar content (mol) of the Group VIIIB elements of the first catalyst in the first reaction chamber is achieved in the first reactor.

[0052] In one example, a diluent gas may be provided simultaneously with the feed gas into the first reaction zone or first reactor.

[0053] In one example of the apparatus described herein, the inlet of the first reactor is connected to a pressurized gas storage vessel holding the feed gas and a diluent gas source, wherein the feed gas and the diluent gas flow rates are controlled by flow controlling devices so that a specific initial ratio between volumetric flow rate (L/min) and molar content (mol) of the Group VIIIB elements of the first catalyst in the first reaction chamber is achieved in the first reactor.

[0054] In one example of the method described herein, the feed gas and the diluent gas are mixed in a controlled manner using flow controlling devices to obtain a specific initial ratio between volumetric flow rate (L/min) and molar content (mol) of the Group VIIIB elements of the first catalyst.

[0055] In one example, the initial ratio between volumetric flow rate and molar content (mol) of the Group VIIIB elements of the first catalyst in the first reaction chamber is between about 5 L/min/mol to about 100 L/min/mol.

[0056] In one example of the method described herein, the quantity of the feed gas is controlled to obtain a volumetric flow rate (L/min), and wherein an initial ratio between volumetric flow rate and molar content (mol) of the Group VIIIB elements of the first catalyst in the first reaction chamber is between about 5 L/min/mol to about 100 L/min/mol.

[0057] In one example of the method described herein, the quantities of the feed gas and the diluent gas are controlled to obtain a volumetric flow rate (L/min), and wherein an initial ratio between volumetric flow rate and molar content (mol) of the Group VIIIB elements of the first catalyst in the first reaction chamber is between about 5 L/min/mol to about 100 L/min/mol.

[0058] In one example of the apparatus described herein, the inlet of the first reactor is connected to a pressurized gas storage vessel holding the feed gas, wherein the quantity of feed gas is controlled by a flow controlling device so that an initial ratio between volumetric flow rate (L/min) and molar content (mol) of the Group VIIIB elements of the first catalyst of between about 5 L/min/mol to about 100 L/min/mol is achieved in the first reactor.

[0059] In one example of the apparatus described herein, the inlet of the first reactor is connected to a pressurized gas storage vessel holding the feed gas and a diluent gas source, wherein the quantities of feed gas and diluent gas are controlled by separate flow controlling devices so that an initial ratio between volumetric flow rate (L/min) and molar content (mol) of the Group VIIIB elements of the first catalyst of between about 5 L/min/mol to about 100 L/min/mol is achieved in the first reactor. In one example, the feed gas (with or without diluent gas) is contacted with a first catalyst bed heated to a desired reaction temperature in a reaction zone, whereby the temperature is sufficient for providing the energy for the partial catalytic decomposition of hydrocarbons in the feed gas. In one example, the temperature of the first catalyst bed is between about 500 °C to about 650 °C, between about 600 °C to about 750 °C, between about 700 °C to about 850 °C, or between about 800 °C to about 950 °C. In one example, the temperature of the first catalyst bed is between about 600 °C to about 750 °C. In one example, the temperature of the first catalyst bed is between about 650 °C to about 750 °C. In one example, the temperature in the first reaction zone (or first reactor) is between about 500 °C to about 900 °C.

[0060] In one example, the contacting of the feed gas (with or without diluent gas) with the first catalyst heated bed may occur continuously. In one example, the contacting of the feed

gas (with or without diluent gas) with the first catalyst heated bed may occur for up to about 1 hour, about 2 hours, about 3 hours, about 4 hours, about 5 hours, about 6 hours, about 7 hours, about 8 hours, about 9 hours, about 10 hours, about 20 hours, about 40 hours, or more, depending on the reactor size, catalyst loading and volumetric flow rate. In one example, the contacting of the feed gas (with or without diluent gas) with the first catalyst heated bed may occur for up to about 5 hours, depending on the reactor size, catalyst loading and volumetric flow rate. In one example, the contacting of the feed gas (with or without diluent gas) with the first catalyst heated bed may occur for up to about 3 hours, depending on the reactor size, catalyst loading and volumetric flow rate.

[0061] The first catalyst and the second catalyst can be fabricated from transition metal salts, for example Groups IVB to VIIIB, IB and IIB; or non-transition metal salts, for example, Groups IIA and IIIA. In one example, the first catalyst and the second catalyst are independently selected from elements consisting of Groups IVB to VIIIB, IB, IIB, IIA and IIIA, or combinations thereof.

[0062] In one example, the first catalyst can be selected from a group consisting of Groups IVB to VIIIB, IB, IIB, IIA and IIIA, or combinations thereof. In one example, the second catalyst can be selected from a group consisting of Groups IVB to VIIIB, IB, IIB, IIA and IIIA, or combinations thereof. In one example, the catalyst (either the first catalyst or the second catalyst) contains transition metals from VIIIB group. In one example, the second catalyst has a lower Group VIIIB metal loading content than the first catalyst. In one example, the first catalyst is either: (a) 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO; or (b) 26 wt.% Fe, 14 wt.% Ni, 10 wt.% 10Mo and 50 wt.% MgO. In another example, the second catalyst is 3 wt.% Co, 2 wt.% Mo and 95 wt.% MgO.

[0063] In one example, the catalyst of the present disclosure is in a reduced form. In one example, the catalyst of the present disclosure is in an oxidized form. In one example, the catalyst can be reduced prior to the partial decomposition in the flow of gas comprising of hydrogen.

[0064] In one example, the first catalyst (catalyst in the first reactor) or second catalyst (catalyst in the second reactor) may be reduced. Without being bound by theory, it is believed that the reduction of these catalysts may be achieved by heating the catalyst at a temperature between about 200 °C to about 700 °C. In one example, the catalyst may be reduced at between about 200 °C to about 350 °C, about 300 °C to about 450 °C about 400 °C to about 550 °C, about 500 °C to about 650 °C, or about 600 °C to about 700 °C. In one example, the catalyst may be

reduced at about 600 °C. The heating of the catalyst for the reduction of the catalyst may be performed for up to about 5 hours. In one example, the heating of the catalyst for the reduction of the catalyst is performed for up to about 1 hour. In one example, the heating of the catalyst for the reduction of the catalyst may be performed for up to about 1 hour, about 2 hours, about 3 hours, about 4 hours, or about 5 hours. The heating of the catalyst for the reduction of the catalyst may be performed using a reducing gas. The reducing gas may be any gas or gas mixtures which is able to convert metal oxides of Group VIIIB into metallic form. In one example, the reducing gas may be selected from a group consisting of hydrogen, carbon monoxide, hydrocarbons, and any combinations thereof.

[0065] In one example, the reduction of the catalyst may be performed using between about 0.01 L/min to about 0.5 L/min of reducing gas per 1 g of catalyst. In one example, the reduction of the catalyst may be performed using between about 0.01 L/min to about 0.5 L/min of reducing gas with about 0.01 L/min to about 0.5 L/min of diluent gas mixture per 1 g of catalyst.

[0066] In one example, the catalyst may be reduced under about 0.1 L/min reducing gas and about 0.1 L/min diluent gas mixture for about 4.5 g of catalyst. In one example, the catalyst may be reduced under about 0.1 L/min hydrogen gas and about 0.1 L/min diluent gas mixture for about 4.5 g of catalyst. In one example, the catalyst may be reduced under about 0.1 L/min reducing gas and about 0.1 L/min nitrogen gas mixture for about 4.5 g of catalyst. In one example, the catalyst may be reduced under about 0.1 L/min hydrogen gas and about 0.1 L/min nitrogen gas mixture for about 4.5 g of catalyst.

[0067] It is known in the art that upon contacting a mixture of feed gas which contains hydrocarbon mixtures with a catalyst, selective decomposition of unsaturated hydrocarbons (for example, but not limited to, olefins) occurs (Veksha et al., 2017; Jia et al., 2020). The decomposition can be partial, meaning that less than 100% of hydrocarbons containing in the feed gas (paraffins and/or olefins) are decomposed. The catalyst undergoes deactivation during this process and the decomposition efficiency of hydrocarbons can decrease over time.

[0068] In an example of the present disclosure, when the feed gas (with or without the diluent gas) is contacted with the first catalyst, the feed gas undergoes partial decomposition yielding the intermediate gas. In one example, the partial decomposition of feed gas can be described by the following reaction: $C_xH_y = xC + 0.5yH_2$, where x and y are the number of carbon and hydrogen atoms in a hydrocarbon compound, respectively. The challenging part is to maintain the activity of the catalyst in order to decompose unsaturated hydrocarbons for a prolonged duration and provide an intermediate gas with consistent properties. The changes in

intermediate gas properties can result in different properties of CNT being produced (such as enlargement of CNT diameter or formation of non-filamentous spherical carbon particles, contaminating the product).

[0069] The influence of initial ratio (i.e. within the first 5 minutes of reaction) between volumetric flow rate, V_f (L/min), and the molar content of transition metals from group VIIIB, n (mol), in the first reaction chamber on intermediate gas composition is shown using two catalysts, containing 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO (denoted as 40Co-10Mo) and 26 wt.% Fe, 14 wt.% Ni, 10 wt.% Mo and 50% MgO (denoted as 26Fe-14Ni-10Mo). In both cases, the mass of catalyst is the same (4.5 g) and the catalytic decomposition of gas is conducted at about 700 °C. The diluent N_2 gas flow rate is fixed at 0.4 L/min while the ratio of volumetric feed gas flow rate V_f (L/min) to the molar amount of transition metals from group VIIIB (here, Co or Fe+Ni, respectively), $n(\text{Co})$ and $n(\text{Fe+Ni})$, is varied. The composition of intermediate gas exiting the first reactor (Reactor 1) is shown in FIG. 8. Regardless of the V_f/n values, the content of paraffins in intermediate gas fluctuated between approximately 3 vol.% to approximately 9 vol.%, suggesting little if any effect on the paraffin partial decomposition. However, the outcome is different in case of olefins. At low initial V_f/n values, the catalysts are more effective during the partial decomposition of olefins, compared to the high V_f/n values. In this respect, the inventors of the present disclosure have found that the V_f/n ratio may be a useful parameter for controlling the content of unsaturated hydrocarbons in the intermediate gas, which is important for the selective synthesis of small diameter CNTs, and to avoid the formation of non-filamentous carbon. Both 40Co-10Mo and 26Fe-14Ni-10Mo catalysts have comparable catalytic activities during this process.

[0070] Thus, in one example, the activity of the first catalyst or the catalyst in the first reactor can be maintained by controlling the volumetric gas feed flow rate, V_f (L/min), to the amount of the molar content of transition metals from group VIIIB, n (mol). The initial V_f/n values in the first reaction chamber can be maintained between about 5 L/min/mol to about 100 L/min/mol. In one example, the initial V_f/n value in the first reaction chamber is between 10 to about 40 L/min/mol. Without being bound by theory, it is believed that the method and/or apparatus of the present disclosure may use the initial V_f/n value of about 5 L/min/mol to about 25 L/min/mol, about 20 L/min/mol to about 45 L/min/mol, about 40 L/min/mol to about 65 L/min/mol, about 60 L/min/mol to about 85 L/min/mol, or about 80 L/min/mol to about 100 L/min/mol.

[0071] In one example, FIG. 2A shows the resulting CNTs from the partial decomposition of the feed gas in the first reactor (Reactor 1) over the 40Co-10Mo catalyst. It can be seen that the decomposition of feed gas resulted in the formation of multi-walled CNTs which are predominantly more than 10 nm in outer diameter. FIG. 2B shows that about > 98% of characterized CNTs had outer diameters in the range between about 10 nm to about 40 nm. The multi-walled CNT yield after about 90 minutes of reaction was about 13 ± 4 g per 1 g of the first catalyst and the conversion efficiency of plastic feed was about $8 \% \pm 2 \%$.

[0072] In one aspect, the invention provides an intermediate gas composition obtained by the preferred embodiments of the method and/or apparatus disclosed herein. In one example, the intermediate gas comprises C₁-C₅ hydrocarbon compounds, and hydrogen. In another example, the intermediate gas comprises C₁-C₅ hydrocarbon compounds, CO, CO₂, and hydrogen.

[0073] In one example, the ratio of paraffins to olefins in the intermediate gas varies between about 1 to about 50. For example, the ratio of paraffins to olefins in the intermediate gas can be between about 1 to about 2.5, between about 2 to about 3.5, between about 3 to about 4.5, between about 4 to about 5.5, between about 5 to about 6.5, between about 6 to about 7.5, between about 7 to about 8.5, between about 8 to about 9.5, between about 9 to about 10.5, between about 10 to about 25, between about 20 to about 35, between about 30 to about 45, between about 40 to about 55, between about 50 to about 65, between about 60 to about 75, or between about 70 to about 95. In one example, the ratio of paraffins to olefins in the intermediate gas varies between about 2.4 to about 47. In one example, the ratio of paraffins to olefins in the intermediate gas is about 2.4. In one example, the ratio of paraffins to olefins in the intermediate gas is about 3.7. In one example, the ratio of paraffins to olefins in the intermediate gas is about 47.

[0074] In one example, the intermediate gas comprises a mixture of one or more gases, selected from methane, ethane, ethylene, propane, propylene, propadiene, methylacetylene, n-butane, 1-butene, cis-2-butene, 2-methyl-2-butene, cis-2-pentene, 1-pentene, hydrogen, carbon monoxide, carbon dioxide, and combinations thereof.

[0075] In one example, the intermediate gas comprises up to about 30 vol.% of methane.

[0076] In one example, the intermediate gas comprises up to about 10 vol.% of ethane.

[0077] In one example, the intermediate gas comprises up to about 5 vol.% of ethylene.

[0078] In one example, the intermediate gas comprises up to about 5 vol.% of propane.

[0079] In one example, the intermediate gas comprises up to about 5 vol.% of propylene.

[0080] In one example, the intermediate gas comprises up to about 5 vol.% of propadiene.

[0081] In one example, the intermediate gas comprises up to about 5 vol.% of methylacetylene.

[0082] In one example, the intermediate gas comprises up to about 5 vol.% of n-butane.

[0083] In one example, the intermediate gas comprises up to about 5 vol.% of 1-butene.

[0084] In one example, the intermediate gas comprises up to about 5 vol.% of cis-2-butene.

[0085] In one example, the intermediate gas comprises up to about 5 vol.% of 2-methyl-2-butene.

[0086] In one example, the intermediate gas comprises up to about 5 vol.% of cis-2-pentene.

[0087] In one example, the intermediate gas comprises up to about 5 vol.% of 1-pentene.

[0088] In one example, the intermediate gas comprises up to about 90 vol.% of hydrogen.

[0089] In one example, the intermediate gas comprises up to about 5 vol.% of carbon monoxide.

[0090] In one example, the intermediate gas comprises up to about 5 vol.% of carbon dioxide.

[0091] In one example, the intermediate gas comprises of methane (between about 3 vol.% to about 7 vol.%), ethane (between about 0.5 vol.% to about 1.5 vol.%), ethylene (between about 0.01 vol.% to about 2 vol.%), propane (between about 0.01 vol.% to about 0.05 vol.%), propylene (between about 0.01 vol.% to about 2 vol.%), propadiene (between about 0.01 vol.% to about 0.04 vol.%), methylacetylene (between about 0.01 vol.% to about 0.15 vol.%), n-butane (between about 0.01 vol.% to about 0.03 vol.%), 1-butene (between about 0.01 vol.% to about 0.04 vol.%), cis-2-butene (between about 0.01 vol.% to about 1 vol.%), 2-methyl-2-butene (between about 0.01 vol.% to 0.03 vol.%), cis-2-pentene (between about 0.01 vol.% to 0.05 vol.%), 1-pentene (between about vol.% 0.01 to about 0.06 vol.%), hydrogen (between about 25 vol.% to about 55 vol.%), carbon monoxide (between about 0.1 vol.% to about 5 vol.%) and carbon dioxide (between about 0.01 vol.% to about 1 vol.%).

[0092] In one example, the concentrations of paraffins in the intermediate gas, which serve as the feedstock for the growth of small diameter CNTs, may be between about 2 vol.% to about 85 vol.%. In one example, the concentrations of paraffins in the intermediate gas may be between about 2 vol.% to about 15 vol.%, about 10 vol.% to about 25 vol.%, about 20 vol.% to about 35 vol.%, about 30 vol.% to about 45 vol.%, about 40 vol.% to about 55 vol.%, about 50 vol.% to about 65 vol.%, about 60 vol.% to about 75 vol.%, or about 70 vol.% to about 65 vol.%. In one example, the concentrations of paraffins in the intermediate gas, which serve as the feedstock for the growth of small diameter CNTs, may be between about 4.7 vol.% to about 8.3 vol.%.

[0093] In one example, the concentrations of olefins in the intermediate gas, which serve as the feedstock for the growth of small diameter CNTs, may be between about 0.01 vol.% to about 15 vol.%. In one example, the concentrations of olefins in the intermediate gas may be between about 0.01 vol.% to about 0.05 vol.%, about 0.04 vol.% to about 1.0 vol.%, about 0.9 vol.% to about 1.5 vol.%, about 1 vol.% to about 2.5 vol.%, about 2 vol.% to about 3.5 vol.%, about 3 vol.% to about 4.5 vol.%, about 4 vol.% to about 5.5 vol.%, about 5 vol.% to about 6.5 vol.%, about 6 vol.% to about 7.5 vol.%, about 7 vol.% to about 8.5 vol.%, about 8 vol.% to about 9.5 vol.%, about 9 vol.% to about 10.5 vol.%, about 10 vol.% to about 11.5 vol.%, about 11 vol.% to about 12.5 vol.%, about 12 vol.% to about 13.5 vol.%, about 13 vol.% to about 14.5 vol.%, or about 14 vol.% to about 15.5 vol.%. In one example, the concentrations of olefins in the intermediate gas, which serve as the feedstock for the growth of small diameter CNTs, may be between about 0.1 vol.% to about 3.5 vol.%

[0094] In one example, Table 2 shows the composition of intermediate gas exiting the first reactor (Reactor 1) over the 40Co-10Mo catalyst and measured immediately after the termination of CNT synthesis (based on 6 runs). The gas contained C₁-C₅ hydrocarbons, CO, CO₂, H₂ and N₂. The concentrations of paraffins and olefins varied in the ranges of between about 4.7 vol.% to about 8.3 vol.% and between about 0.1 vol.% to about 3.5 vol.%, respectively. Among the analyzed C₁-C₅ hydrocarbons, the concentration of methane is the highest (at about 4.0 vol.% to about 7.1 vol.%). According to the results in Table 2, the total content of hydrocarbon compounds in the intermediate gas is lower compared to the feed gas (listed in Table 1). In these experiments, prior to being provided into Reactor 1, about 1.0 to about 1.2 L/min of feed gas is diluted with about 0.4 L/min of diluent gas (N₂). However, the observed changes in gas composition could not be attributed solely to the dilution effect, since in that case, the concentrations of all gas components would decrease proportionally. The inventors of the present disclosure have thus shown the decrease in the concentration of olefins of the feed gas compared to the paraffins is more pronounced using the method and/or apparatus of the present disclosure. These data are ascribed to the higher reactivity of olefins compared to paraffins (especially, methane) at the reaction conditions. As a result of preferential decomposition of unsaturated hydrocarbons using the method and/or apparatus of the present disclosure, in one example, the paraffins/olefins ratios increased to between about 2.4 to about 47 and in another example, the H₂ content in the intermediate gas increased to between about 30.1 vol.% to about 48.9 vol.%.

[0095] In one example, the intermediate gas as described herein is then subjected to the conditions in a next reaction zone (such as, a next reactor) as described herein. In one example, the intermediate gas is separated from the solid carbon and first catalyst before being provided into the second reaction zone. In one example, any solid products (if any), may be separated by any suitable separation method such as, but not limited to, a filter or cyclone reactor. In one example the intermediate gas exiting the first reactor (or first reaction zone), can be immediately transferred through a gas line into the second reactor or stored. In one example, the connection between the first reactor and the second reactors further comprises a particle filtration device and/or a pressure regulator. In one example, the connection between the first reactor and the second reactors further comprises a particle filtration. In one example, the connection between the first reactor and the second reactors further comprises a pressure regulator. In one example, the connection between the first reactor and the second reactors further comprises a particle filtration device and a pressure regulator.

[0096] In one example, the intermediate gas is contacted with the second catalyst in the second reaction zone (or second reactor).

[0097] In one example, the intermediate gas is contacted with a catalyst bed heated to a desired reaction temperature in a second reaction zone (or second reactor), whereby the temperature is sufficient to initiate the catalytic decomposition of hydrocarbons containing in the intermediate gas into small diameter CNTs. In one example, the temperature of the catalyst bed (in the second reaction zone) is between about 500 °C to about 650 °C, between about 600 °C to about 750 °C, between about 700 °C to about 850 °C, between about 800 °C to about 950 °C, between about 900 °C to about 1050 °C, between about 1000 °C to about 1200 °C. In one example, the temperature of the catalyst bed (in the second reaction zone) is about 600 °C to about 1200 °C. In one example, the temperature of the catalyst bed (in the second reaction zone) is about 1100 °C. In one example, the temperature of the catalyst bed (in the second reaction zone) is about 1000 °C.

[0098] In one example, the contacting of the intermediate gas with the catalyst heated bed in the second reaction zone may occur continuously. In one example, the contacting of the intermediate gas with the catalyst heated bed in the second reaction zone may occur for up to about 10 minutes, up to about 1 hour, up to about 2 hours, up to about 3 hours, up to about 4 hours, up to about 5 hours, up to about 6 hours, up to about 7 hours, up to about 8 hours, up to about 9 hours, up to about 10 hours, up to about 20 hours, up to about 40 hours, or more, depending on the reactor size, catalyst loading and volumetric flow rate. In one example, the

contacting of the intermediate gas with the catalyst heated bed in the second reaction zone may occur for up to about 5 hours, depending on the reactor size, catalyst loading and volumetric flow rate. In one example, the contacting of the intermediate gas with the catalyst heated bed in the second reaction zone may occur for up to about 3 hours, depending on the reactor size, catalyst loading and volumetric flow rate. In one example, the contacting of the intermediate gas with the catalyst heated bed in the second reaction zone may occur for up to about 10 minutes, depending on the reactor size, catalyst loading and volumetric flow rate.

[0099] In one example, the intermediate gas exiting the first reactor (Reactor 1) is transferred through a gas line into the next reactor (Reactor 2) which is filled with the catalyst containing 3 wt.% Co, 2 wt.% Mo and 95 wt.% MgO (denoted as 3Co-2Mo) for about 20 minutes of synthesis. FIG. 3A illustrates images of CNT bundles produced in Reactor 2 taken by TEM. Area 1 and Area 2 of the analyzed sample show magnified images of CNTs from different spots of the specimen (FIG. 3B to 3F). The sample contained CNTs with outer diameters of about several nm and with as little as three walls. FIG. 3D shows the outer diameter of CNTs measured from TEM images. Approximately 95% of CNTs had outer diameters between about 1 nm to about 7 nm. The number of CNTs with outer diameters between about 1 nm to about 5 nm is about 82%, and the number of CNTs with outer diameters between about 3 nm to about 4 nm is about 24%. The yield of small diameter CNTs is about 0.18 ± 0.09 g per 1 g of the second catalyst and the conversion efficiency of plastic feed is about $0.049\% \pm 0.015\%$. These yields are lower compared to the yields of multi-walled CNTs produced in Reactor 1. In all 6 runs, small diameter CNTs are produced suggesting the suitability of obtained intermediate gas from Reactor 1 for the synthesis of small diameter CNTs.

[0100] Considering similar catalytic activities of two catalysts, the effect of V_f/n on the intermediate gas composition over reaction time is investigated using only 40Co-10Mo in one example as follows: The evolution of paraffins and olefins in the intermediate gas is shown in FIG. 9. At higher initial V_f/n values (samples 1 and 2 at about 61 L/min/mol and about 49 L/min/mol, respectively), the concentration of olefins in the intermediate gas rapidly increased. This could be attributed to the deactivation of catalyst in the excess of hydrocarbon compounds present in the feed gas. On the other hand, when the initial V_f/n values are kept low (samples 3, 4, 5 and 6 at about 35 L/min/mol, about 36 L/min/mol, about 32 L/min/mol and about 30 L/min/mol, respectively), the catalyst in the first reaction zone has sufficient activity for the decomposition of olefins and the concentration of olefins in intermediate gas could be maintained below about 4 vol.% for at least about 95 minutes. The V_f/n value has little effect

on the concentration of paraffins. This is likely due to the higher selectivity of the catalysts towards the partial decomposition of olefins as explained above. According to the shown data of this example, the production time of the intermediate gas composition for the synthesis of small diameter CNTs can be increased by decreasing the V_f/n values. For example, to produce intermediate gas with low content of olefins for longer time, the V_f/n values may be maintained at between about 10 L/min/mol to about 40 L/min/mol for about 95 minutes of gas production. The inventors of the present disclosure have managed to show that the adjustment of the ratio between V_f and the molar content of transition metals from group VIIIB in the catalyst allows for the convenient generation of intermediate gas in Reactor 1 for the growth of small diameter CNTs.

[0101] The inventors of the present disclosure have demonstrated that it is beneficial to manufacture CNTs in multiple steps. In one example of the present disclosure, the multiple step method comprises at least the following two-steps:

Step (a): flowing the feed gas into a first reactor (Reactor 1) containing a first catalyst, wherein a portion of the feed gas is partially decomposed into an intermediate gas and solid carbon; and

Step (b): flowing the intermediate gas into a second reactor (Reactor 2) containing a second catalyst, wherein a portion of the intermediate gas is converted into small diameter CNTs.

[0102] In one example, when the feed gas is diluted and used for Step (b) without Step (a), it preferentially yields non-filamentous carbon over the catalyst. When feed gas is not diluted and is used directly for Step (b) omitting the Step (a), it undergoes non-catalytic thermal cracking into spherical soot and/or carbon black particles. This is likely due to the low thermal stability of some of the hydrocarbon compounds in the feed gas at temperatures required for small diameter CNT synthesis. Thus, in this example, having the Step (a) prior to the Step (b) allows for selective catalytic decomposition of hydrocarbons at lower temperature and avoidance of non-filamentous carbon formation at higher temperature used for small diameter CNT synthesis.

[0103] In one example, in order to investigate how the growth of small diameter CNTs is influenced by dilution of hydrocarbons (i.e. due to the addition of N_2 and formation of H_2 during the conversion of feed gas into intermediate gas), the feed gas (about 0.2 L/min) is mixed with N_2 (about 1.9 L/min N_2) and then supplied directly into Reactor 2 containing the 3Co-2Mo catalyst at about 1000 °C (in this example, the Reactor 1 is not used). The

composition of diluted feed gas is analyzed by gas chromatography and is provided in FIG. 5 (“Diluted feed gas”). In this example, the concentrations of all hydrocarbon gases decrease proportionally after the dilution of feed gas. The contents of paraffins and olefins is about 1.4 vol.% and about 4.4 vol.%, respectively, which corresponds to about 10 times dilution. However, the paraffins/olefins ratio is similar to that of the undiluted feed gas, i.e. about 0.31 (refer to Table 1). The detailed composition of hydrocarbon compounds, CO, CO₂ and H₂ in diluted gas is shown in FIG. 5 and compared to the intermediate gas (“Intermediate gas” in Fig. 5) from the experiments described above. One difference of the diluted gas is the high content of olefins, such as ethylene, propylene and c-2-butene, and the low content of methane compared to the intermediate gas. Another difference is the lower content of H₂. The concentration of gases is also analyzed after the synthesis in Reactor 2 (“After using diluted feed gas” and “After using intermediate gas”). In the case of using intermediate gas, the changes in gas composition are within the error range, suggesting low conversion rates of hydrocarbons at experimental conditions. This could be attributed to the low decomposition rate of intermediate gas due to the high stability of gas components (especially, methane). On the other hand, when diluted feed gas is used in Reactor 2, the decomposition of hydrocarbon compounds (especially, ethylene, propylene and cis-2-butene) is observed and this process is accompanied by hydrogen formation, suggesting the higher reactivity of the components in the diluted feed gas. In this example, the inventors of the present disclosure have discovered that even though the concentrations of hydrocarbon compounds could be decreased by dilution, there are considerable differences in the decomposition behaviour, occurring in Reactor 2.

[0104] In another example, FIG. 6 shows the morphology of carbon material produced from the diluted feed gas. Non-filamentous coke is the predominant type of carbon in the product. Short CNTs with various diameters from several nm to several tens of nm and carbon fibers are observed in the sample, suggesting that the diluted gas provides low selectivity towards the synthesis of small diameter CNTs. This is probably attributed to the composition of gas. For instance, it could be due to the excess of certain hydrocarbon compounds that preferentially decompose into non-filamentous carbon, carbon fibers and CNTs with various diameters as well as the lack of certain hydrocarbon compounds that preferentially decompose into small diameter CNTs. In this respect, the conversion of feed gas into intermediate gas by means of Reactor 1 is advantageous for the selective synthesis of small diameter CNTs.

[0105] In another example, the importance of producing intermediate gas in Reactor 1 prior to Reactor 2 is further studied using the following experiment. About 0.9 L/min to about 1.8

L/min of feed gas is diluted with about 0.4 L/min of N₂ and supplied directly to Reactor 2 for about 28 minutes (in this case, Reactor 1 is omitted). Reactor 2 is preheated to about 1000 °C, which is the similar temperature to the previous experiments, but the catalyst is omitted. The formation of carbon particles, presumably, soot and/or carbon black is observed in this example. The representative morphology is then characterized by TEM and is shown in FIG. 7. Spherical particles with diameters above about 100 nm and below about 1000 nm are produced, suggesting that at about 1000 °C, the feed gas is prone to non-catalytic decomposition into non-filamentous carbon that can contaminate small diameter CNTs. The high content of olefins in the feed gas may be the reason for the observed soot/carbon black formation. No such carbon is formed when intermediate gas having low content of olefins is used in Reactor 2.

[0106] In another example, it is also demonstrated that it is beneficial when the second catalyst uses a different composition from the first catalyst. It is acceptable to have high transition metal loading on the support in the first catalyst for step (a) in order to maintain high catalytic activity towards the partial decomposition of hydrocarbon compounds. The higher loading however seems to cause metal particle sintering which limits the growth of small diameter CNTs. Therefore, it is preferable to have a catalyst with low metal loading and high metal dispersion for step (b) in order to obtain high selectivity to the growth of CNTs with small diameters.

[0107] In another example, FIG. 10 shows the influence of synthesis duration on the formation of carbon in the two reactors. The mass of carbon is expressed per 1 g of catalyst. As it is shown for feed gas from LPET, at short synthesis time (e.g., about 10 minutes), carbon is mainly deposited in Reactor 1. With longer synthesis time, the loss of catalytic activity of Ni catalyst occurred, which is evidenced by the plateau of carbon mass formed in Reactor 1. As the catalytic activity of Ni catalyst in Reactor 1 decreases, larger quantities of carbon are produced in Reactor 2. After about 30 minutes of the synthesis, the carbon deposition in Reactor 2 is close to that in Reactor 1. The carbon growth from feed gas from HPET resembles the one from LPET. After about 20 minutes of synthesis, the amount of deposited carbon is higher in Reactor 1 compared to Reactor 2. The total quantity of deposited carbon from the gas from HPET is lower compared to the gas from LPET.

[0108] In one example, the sizes of CNTs produced in two reactors are compared by measuring the outer diameters of about 100-200 nanotubes from each sample using TEM images (FIG. 11). Regardless of the synthesis time and feedstock, multi-walled CNTs with outer diameters of about 5 nm to about 35 nm are formed. At each synthesis time, the outer diameters of multi-

walled CNTs synthesized in Reactor 1 and Reactor 2 are observed to be comparable, probably, due to the use of the same catalyst in both reactors. In this respect, different catalysts could be required in Reactors 1 and 2 in order to partially decompose feed gas and selectively produce small diameter CNTs. Representative images of CNTs from two reactors are shown in FIG. 12.

[0109] The method and apparatus as disclosed herein allow for the simple, cost-effective, and selective conversion of the feed gas containing a mixture of multiple hydrocarbons into small diameter CNTs.

[0110] In one aspect, there is provided a small diameter CNT produced by the method and apparatus as disclosed herein. Compared to multi-walled CNTs produced from hydrocarbon gas mixtures by method disclosed in the art, CNTs produced by the method and apparatus of the present disclosure are represented by individual CNTs as well as CNTs agglomerated into bundles. CNTs produced by the method and apparatus of the present disclosure have outer diameters between about 1 nm to about 10 nm (about 95% tubes having outer diameters between about 1 nm to about 7 nm, about 82% tubes having outer diameters between about 1 nm to about 5 nm, about 24% tubes having outer diameters between about 3 nm to about 4 nm), containing tubes with three walls, having radial breathing modes in Raman spectra at wave lengths below about 400 cm^{-1} .

[0111] In one example, the Raman spectroscopy spectrum of small diameter CNTs is shown in FIG. 4A. The peaks at wave lengths of about 1356 cm^{-1} , about 1590 cm^{-1} and about 2680 cm^{-1} correspond to D-, G- and 2D-bands, which are also commonly present in carbon nanomaterials such as multi-walled CNTs and carbon nanosheets. The characteristic feature confirming that the sample contains small diameter CNTs with only few-walls is the presence of radial breathing mode at wave lengths between about 100 cm^{-1} to about 400 cm^{-1} (Flahaut et al., 2005) that can be clearly observed in the inset of FIG. 4A. FIG. 4B shows the temperature programmed oxidation profile of synthesized small diameter CNTs compared to two multi-walled CNT samples, namely, CNTs produced in Reactor 1 during the experiment (outer diameter of about 10 nm to about 40 nm) and commercial CNTs manufactured by Nanografi (outer diameter of about 20 nm to about 30 nm). During heating in oxidizing conditions, the carbon-based samples are converted into CO and CO₂. The decomposition temperature is related to the structure of carbon material. Single-walled CNTs were reported to produce decomposition peak at approximately 510 °C (Kitiyanan et al., 2000). The stability of multi-walled CNTs towards oxidation is generally higher, especially, if contents of catalytic metal impurities and amorphous carbon are low (Cabana et., 2015). Both multi-walled CNT samples

from Reactor 1 and Nanografi shown in FIG. 4B had decomposition peaks at about 650 °C. The small diameter CNTs from Reactor 2 had the single decomposition peak at approximately 560 °C, which is intermediate between the peaks corresponding to single-walled and multi-walled CNTs, suggesting that the CNTs had small diameters.

[0112] In one example, the method may further comprise a step of purifying the CNTs to remove impurities such as, but not limited to catalyst residues. In one example, the CNTs can be purified using methods known in the art, such as but not limited to purification by acids.

[0113] In one example, the method may further comprise a step of capturing the hydrogen emission. In one example, the hydrogen may be further delivered to a vessel, apparatus, or system.

[0114] It should further be understood that the exemplary embodiments are merely examples, and are not intended to limit the scope, applicability, configuration, or operation of the invention described herein in any way. Instead, the detailed description provided above will provide another skilled person in the art with a convenient teaching for implementing an exemplary embodiment of the present invention. It should be appreciated that various changes may be made to the function and arrangement of components and method of operation described in any exemplary embodiment in the present description without departing from the scope of the invention as set forth in the present application (including the claims).

[0115] The invention described herein may also suitably be practiced in the absence of any element or elements, limitation or limitations, which are not specifically disclosed herein. For example, the terms "comprising", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions used herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. It should also be understood that although the present invention has been disclosed by preferred embodiments, preferred examples, and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[0116] The invention has been described broadly and generically. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This would include the generic description of the invention with a proviso or negative

limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[0117] Certain embodiments may have been disclosed in a range format. It should be understood that the description in range format is merely for convenience and for brevity - and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Therefore, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range described. As an example, description of a range such as from 1 to 5 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 5, from 3 to 5, etc., as well as any individual number within that range, for example, 1, 2, 3, 4, and 5. This also applies regardless of the breadth of the range.

TABLES

[0118] Table 1. Typical feed gas composition from plastics (vol. %).

	Mean	Minimum	Maximum	Carbon number
Hydrocarbon compounds				
methane	8.6	7.9	9.4	C1
ethane	3.2	3.0	3.4	C2
ethylene	11.2	10.2	12.3	C2
propane	0.2	0.2	0.3	C3
propylene	15.7	14.7	16.7	C3
propadiene	0.1	B.D.L.	0.3	C3
methyl acetylene	B.D.L.*	B.D.L.	B.D.L.	C3
n-butane	B.D.L.	B.D.L.	B.D.L.	C4
1-butene	0.6	B.D.L.	1.7	C4
cis-2-butene	1.8	B.D.L.	8.8	C4
2-methyl-2-butene	1.3	B.D.L.	1.7	C5
cis-2-pentene	0.4	0.3	0.4	C5
1-pentene	1.9	B.D.L.	2.5	C5
Other gases				
hydrogen	4.0	3.4	4.6	
carbon monoxide	B.D.L.	B.D.L.	B.D.L.	
carbon dioxide	B.D.L.	B.D.L.	B.D.L.	
nitrogen		Balance		
Cumulative hydrocarbon content				
paraffins	12.2	11.5	13.0	C1-C5
olefins	39.6	38.4	41.4	C1-C5
paraffins/olefins ratio	0.31	0.30	0.31	

* B.D.L. – below detection limit.

[0119] Table 2. Composition of intermediate gas (vol. %).

	Mean	Minimum	Maximum	Carbon number
Hydrocarbon compounds				
Methane	5.6	4.0	7.1	C1
Ethane	0.9	0.7	1.2	C2
Ethylene	0.70	0.05	1.16	C2
Propane	0.04	0.02	0.05	C3
propylene	0.60	0.04	1.31	C3
propadiene	0.02	0.01	0.04	C3
methyl acetylene	0.03	B.D.L.*	0.1	C3
n-butane	0.01	B.D.L.	0.02	C4
1-butene	0.01	B.D.L.	0.04	C4
cis-2-butene	0.39	0.03	0.90	C4
2-methyl-2-butene	0.004	B.D.L.	0.02	C5
cis-2-pentene	0.01	B.D.L.	0.03	C5
1-pentene	0.01	B.D.L.	0.05	C5
Other gases				
Hydrogen	38.5	30.1	48.9	
carbon monoxide	1.8	1.1	4.0	
carbon dioxide	0.2	B.D.L.	1.0	
nitrogen		Balance		
Cumulative hydrocarbon content				
paraffins	6.6	4.7	8.3	C1-C5
Olefins	1.8	0.1	3.5	C1-C5
paraffins/olefins ratio	3.7	47.0	2.4	

* B.D.L. – below detection limit.

EXAMPLES

Example 1: Method of synthesis of small diameter CNTs

[0120] The method is based on the catalytic conversion of pyrolysis gas (feed gas) in a first reactor over a first catalyst into the intermediate gas and then using the intermediate gas in a second reactor containing a second catalyst to produce small diameter CNTs, yielding > 95% of CNTs with outer diameters of between about 1 nm to about 7 nm. The product contained CNTs with as little as three walls and was characterized by the presence of radial breathing mode in Raman spectra at wave lengths between about 100 cm⁻¹ to about 400 cm⁻¹.

[0121] A mixture of pure plastics containing polypropylene (70 wt.%, PP), low-density polyethylene (6 wt.%, LDPE) and high-density polyethylene (24 wt.%, HDPE) was used as a

feedstock. About 50 g of plastics was fed into the pyrolysis reactor about every 10 minutes for the duration of experiments. All resins were purchased from Lotte Chemical Titan.

[0122] A system for the conversion of plastics into CNTs is provided in FIG. 1. The first step of the process is thermochemical decomposition of plastics into gas that served as a precursor for the growth of CNTs (1). This was accomplished by pyrolysis of plastics at about 450 °C followed by non-catalytic cracking of volatiles at about 530 °C. The produced products were passed through a condenser (≤ 60 °C) to remove liquid oil. The remaining gas (denoted as “feed gas”) was pressurized in a storage vessel (3) to between about 0.1 bar to about 5 bar(g) using a gas pump (2). This allowed creation of a positive pressure gradient for supplying the gas into the CVD system. The pressurized feed gas was further fed into Reactor 1 filled with the first catalyst (about 4.5 g), where the partial decomposition of feed gas occurred. Flow meter (4) was used to regulate the gas supply. Diluent gas (5) was supplied either concurrently or during heating/cooling stages. Reactor 1 was placed into a three-zone electric furnace (8) heated to about 700 °C. K-type thermocouples in various parts of the reactor and pressure gauge (7) were used to monitor the reaction conditions, while the pressure regulator (6) was used to adjust the pressure in Reactor 1. Approximately 1.0 L/min to approximately 1.2 L/min of feed gas was diluted with about 0.4 L/min of N₂ and supplied to Reactor 1. The gas exiting Reactor 1 (denoted as “intermediate gas”) was passed through a particle filter, where entrained catalyst and carbon particles were separated from the gas. Particle-free intermediate gas was directed into Reactor 2 filled with a second catalyst (0.5 g) and pre-heated to the desired synthesis temperature (about 1000 °C). Reactor 2 was equipped with additional N₂ and H₂ gas lines to supply gases for reactor purging and catalyst reduction. The composition of feed and intermediate gases was characterized by an off-line gas chromatograph (Agilent). In order to investigate the partial decomposition of feed gas, the reaction in Reactor 1 was continued for about 90 min. However, the synthesis in Reactor 2 continued for about 20 minutes and was started simultaneously with the start of partial decomposition of feed gas in Reactor 1.

[0123] The first catalyst consisted of 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO (denoted as 40Co-10Mo) or Fe 26 wt.%, Ni 14 wt.%, Mo 10 wt.% and MgO 50 wt.% (denoted as 26Fe-14Ni-10Mo). Both catalysts were synthesized using a modified method from Aboul-Enein and Awadallah (2018). The second catalyst consisted of Co 3 wt.%, Mo 2 wt.% and MgO 95 wt.% (denoted as 3Co-2Mo) and was synthesized using a modified method from Tang et al. (2001). Both catalysts are reduced at 600 °C for 1 h in 0.1 L/min H₂ and 0.1 L/min N₂ mixture prior to the experimental runs.

[0124] The reported yields of solid carbon produced in Reactor 1 based on 90 minutes reaction were calculated as:

$$Y \text{ (g per 1 g catalyst)} = (m - m_{\text{cat}}) / m_{\text{cat}} \quad (1)$$

Where m is the mass of recovered carbon deposits from Reactor 1 or Reactor 2, containing the catalyst, and m_{cat} is the mass of calcined catalyst loaded into Reactor 1 or Reactor 2.

$$Y \text{ (\% per plastic feed)} = (m - m_{\text{cat}}) \cdot 100 / m_{\text{plastics}} \quad (2)$$

Where m_{plastics} is the mass of plastics used for the synthesis.

[0125] Solid residues from Reactor 2 were boiled with 3M HCl to remove catalyst, filtered, rinsed with deionized water until pH between about 5 to about 6 and dried at about 105 °C. The yield was reported as the ratio between the mass of purified product synthesized during about 20 minutes reaction and calcined catalyst loaded into Reactor 2. Unless otherwise stated, the reported data are collected using acid-washed carbon samples.

Example 2: Method of characterization of CNTs

[0126] The morphology of CNTs was characterized by transmission electron microscopy (TEM, JEOL JEM-1400Plus and TEM JEOL 2010 HR) and field emission scanning electron microscopy (FESEM, JEOL JSM-7600F). Raman spectroscopy was conducted using XploRA PLUS, Horiba Scientific with a 532 nm laser excitation. Temperature programmed oxidation was carried out in about 5 vol.% O₂ and about 80 vol.% N₂ mixture by heating about 2 mg to about 4 mg of sample from ambient temperature to about 900 °C at about 5 °C/min.

Example 3: Methods to determine the role of catalyst in the second reactor

[0127] In this example, feed gas was produced using pyrolysis of plastics, followed by catalytic cracking of hydrocarbons containing in volatile pyrolysis products and condensation of upgraded oil (see FIG.1, “(1) generation of feed gas from plastics”). Two mixtures of plastics containing low and high polyethylene terephthalate (PET) contents (denoted as LPET and HPET, respectively) were used as described in Veksha et al., 2020. The mixtures were composed of flexible monolayer films such as polyethylene, polypropylene and polyamide, and multilayer films. The PET contents for LPET and HPET mixtures was about 11.8% and about 27.5%, respectively. The plastic feedstock (about 50 g per run) was loaded into a stainless steel pyrolysis reactor with an inner diameter (i.d.) of about 8.3 cm. A cracking catalyst such as iron-based catalyst supported on ZSM-5 (7.5 g) was prepared as described in Veksha et al.,

2020 and loaded into a subsequent stainless steel cracking reactor with an internal diameter of about 2.2 cm. Prior to experimental runs, the reactors were purged with about 0.2 L/min of N₂ for about 30 minutes to remove air. The pyrolysis and the catalytic cracking reactors were heated to about 550 °C and about 400 °C, respectively, while purging with N₂. To avoid condensation of pyrolysis products in gas lines, a pipe and connections between the pyrolysis and catalytic cracking reactors were preheated to about 400 °C. The produced pyrolysis products are cooled to about 0 °C to about 5 °C for the collection of pyrolysis oil using two traps. The remaining non-condensable pyrolysis gas (feed gas) was collected in a Tedlar bag and utilized for partial decomposition and CNT synthesis. To study the growth and quality of CNTs, the Reactor 1 and Reactor 2 manufactured from quartz were filled with a catalyst comprising NiO (Ni content of about 0.9 wt.%) and CaCO₃ prepared as described in Veksha et al., 2020 (about 1.0 g and about 0.5 g of catalyst, respectively). The reactors are heated to about 700 °C in about 0.1 L/min of N₂. Once the desired temperature was reached, the feed gas from Tedlar bag was pumped at about 0.1 L/min through the CVD reactors for about 10 minutes, about 20 minutes or about 30 minutes. The ratio between volumetric flow rate and Ni molar content in Reactor 1, V_f/n , was about 652 L/min/mol.

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CLAIMS

1. A method of producing small diameter carbon nanotubes from a feed gas obtained by heating a polyolefin-containing feedstock, comprising the steps of:
 - (a) flowing the feed gas into a first reaction zone containing a first catalyst, wherein a portion of the feed gas is partially decomposed into an intermediate gas and solid carbon; and
 - (b) flowing the intermediate gas into a second reaction zone containing a second catalyst, wherein a portion of the intermediate gas is converted into small diameter carbon nanotubes.
2. The method of claim 1, wherein the first catalyst and the second catalyst are independently selected from elements consisting of Groups IVB to VIIIB, IB, IIB, IIA and IIIA, or combinations thereof.
3. The method of claims 1 or 2, wherein step 1(a) further comprises simultaneously flowing a diluent gas into the first reaction zone.
4. The method of claim 2, wherein quantity of the feed gas is controlled to obtain a volumetric flow rate (L/min), and wherein an initial ratio between volumetric flow rate and molar content (mol) of the Group VIIIB elements of the first catalyst in the first reaction chamber is between about 5 L/min/mol to about 100 L/min/mol.
5. The method of claim 3, wherein quantities of the feed gas and the diluent gas are controlled to obtain a volumetric flow rate (L/min), and wherein an initial ratio between volumetric flow rate and molar content (mol) of the Group VIIIB elements of the first catalyst in the first reaction chamber is between about 5 L/min/mol to about 100 L/min/mol.
6. The method of any one of claims 1 to 5, wherein the first catalyst comprises either: (a) 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO; or (b) 26 wt.% Fe, 14 wt.% Ni, 10 wt.% 10Mo and 50 wt.% MgO.
7. The method of any one of claims 1 to 6, wherein temperature in the first reaction zone is between about 500 °C to about 900 °C.

8. The method of any one of claims 1 to 7, wherein the second catalyst is 3 wt.% Co, 2 wt.% Mo and 95 wt.% MgO.
9. The method of any one of claims 1 to 8, wherein temperature in the second reaction zone is between about 600 °C to about 1200 °C.
10. The method of any one of claims 1 to 9, wherein the second catalyst has a lower Group VIIIB metal loading content than the first catalyst.
11. The method of any one of claims 1 to 10, wherein the feed gas and the intermediate gas comprises at least one or more paraffins and one or more olefins.
12. The method of any one of claims 1 to 11, wherein the polyolefin-containing feedstock comprises one or more polyolefins selected from the group consisting of polyethylene, polypropylene, polymethylpentene, polybutene-1, ethylene-octene copolymers, olefin block copolymers, propylene-butane copolymers, polyisobutylene, poly(a-olefin)s, ethylene propylene rubber, ethylene propylene diene monomer rubber, or combinations thereof.
13. A small diameter carbon nanotube produced by the method of any one of claims 1 to 12.
14. An apparatus for production of small diameter carbon nanotubes, the apparatus comprising:
 - a first reactor which is connected to a second reactor in series; wherein
 - the first reactor is configured to hold a first heated catalyst bed comprising a first catalyst, wherein the first catalyst bed generates an intermediate gas and solid carbon when the first catalyst bed is in contact with a feed gas received from an inlet; and
 - the second reactor is configured to hold a second heated catalyst bed comprising a second catalyst, wherein the second catalyst bed generates the small diameter carbon nanotubes when the second catalyst bed is in contact with the intermediate gas received from the first reactor.

15. The apparatus of claim 14, wherein the first catalyst in the first heated catalyst bed and the second catalyst in the second heated catalyst bed are independently selected from elements consisting of Groups IVB to VIIIB, IB, IIB, IIA and IIIA, or combinations thereof.
16. The apparatus of claim 15, wherein the inlet of the first reactor is connected to a pressurized gas storage vessel holding the feed gas, wherein the quantity of feed gas is controlled by a flow controlling device so that
an initial ratio between volumetric flow rate (L/min) and molar content (mol) of the Group VIIIB elements of the first catalyst of between about 5 L/min/mol to about 100 L/min/mol is achieved in the first reactor.
17. The apparatus of claim 15, wherein the inlet of the first reactor is connected to a pressurized gas storage vessel holding the feed gas and a diluent gas source, wherein the quantities of feed gas and diluent gas are controlled by separate flow controlling devices so that
an initial ratio between volumetric flow rate (L/min) and molar content (mol) of the Group VIIIB elements of the first catalyst of between about 5 L/min/mol to about 100 L/min/mol is achieved in the first reactor.
18. The apparatus of any one of claims 14 to 17, wherein the connection between the first reactor and the second reactor further comprises a particle filtration device and/or a pressure regulator.
19. The apparatus of any one of claims 14 to 18, wherein the first catalyst comprises either:
(a) 40 wt.% Co, 10 wt.% Mo and 50 wt.% MgO; or (b) 26 wt.% Fe, 14 wt.% Ni, 10 wt.% 10Mo and 50 wt.% MgO.
20. The apparatus of any one of claims 14 to 19, wherein the second catalyst comprises 3 wt.% Co, 2 wt.% Mo and 95 wt.% MgO.