

REMOVING CARBON NANOTUBES FROM A CONTINUOUS REACTOR EFFLUENT

RELATED APPLICATIONS

5 [0001] The present provisional application is related to United States Patent Application Serial No. 13/263,311 by Noyes and titled "Method for Producing Solid Carbon by Reducing Carbon Oxides," which was filed 06 October 2011, which claims priority based on International Patent Application Number PCT/US2010/029934, by Noyes, entitled "Method for Producing Solid Carbon by
10 Reducing Carbon Oxides," which was filed on 05 April 2010, which in turn claims priority based on United States Provisional Patent Application Serial No. 61/170,199 filed 17 April 2009 and titled "Method for Producing Solid Carbon by Reducing Carbon Oxides," the disclosures of all of which are incorporated herein by this reference.

FIELD

15 [0002] The present techniques relate to an industrial scale process for making carbon nanotubes. Specifically, the techniques are focused on removing carbon nanotubes from a continuous reactor effluent stream.

BACKGROUND

20 [0003] This section is intended to introduce various aspects of the art, which may be associated with exemplary embodiments of the present techniques. This discussion is believed to assist in providing a framework to facilitate a better
25 understanding of particular aspects of the present techniques. Accordingly, it should be understood that this section should be read in this light, and not necessarily as admissions of prior art.

[0004] Materials formed predominately of solid or elemental carbon have been used in numerous products for many years. For example, carbon black is a high
30 carbon content material used as a pigment and reinforcing compound in rubber and

plastic products, such as car tires. Carbon black is usually formed by the incomplete thermal pyrolysis of hydrocarbons, such as methane or heavy aromatic oils.

Thermal blacks, formed by the pyrolysis of natural gas, include large unagglomerated particles, for example, in the range of 200-500 nm in size, among
5 others. Furnace blacks, formed by the pyrolysis of heavy oils, include much smaller particles, in the range of 10-100 nm in size, that agglomerate or stick together to form structures. In both cases, the particles may be formed from layers of graphene sheets that have open ends or edges. Chemically, the open edges form reactive areas that can be used for absorption, bonding into matrices, and the like.

10 [0005] More recent forms of elemental carbon, such as fullerenes, have been developed, and are starting to be developed in commercial applications. In contrast to the more open structures of carbon black, fullerenes are formed from carbon in a closed graphene structure, i.e., in which the edges are bonded to other edges to form spheres, tubes, and the like. Two structures, carbon nanofibers and carbon
15 nanotubes, have numerous potential applications, ranging from batteries and electronics to the use in concrete in the construction industry. Carbon nanomaterials may have a single wall of graphene or multiple nested walls of graphene or form a fiber structure from a stacked set of sheets in a cup or plate form. The ends of the carbon nanotubes are often capped with hemispherical structures, in a fullerene-like
20 configuration. Unlike for carbon black, large scale production processes have not been implemented for carbon nanomaterials. However, research has been conducted on a number of proposed production processes.

[0006] Arc-based, laser-based ablation techniques and chemical vapor deposition have classically been used to generate carbon nanotubes from a carbon surface.

25 For example, techniques for generating carbon nanotubes are reviewed in Karthikeyan, et al., "Large Scale Synthesis of Carbon Nanotubes," E-Journal of Chemistry, 2009, 6(1), 1-12. In one technique described, an electric arc is used to vaporize graphite from electrodes in the presence of metal catalysts, achieving production rates of about 1 gram/minute. Another technique described uses laser
30 ablation to vaporize carbon from a target electrode in an inert gas stream. However,

the laser technique uses high purity graphite and high power lasers, but provides a low yield of carbon nanotubes, making it impractical for large scale synthesis. A third technique described by the authors is based on chemical vapor deposition (CVD), in which a hydrocarbon is thermally decomposed in the presence of a catalyst. In some studies, these techniques have achieved production rates of up to a few kilograms/hour at a 70 % purity level. However, none of the processes described are practical for large scale commercial production.

[0007] Hydrocarbon pyrolysis is used in the production of carbon black and various carbon nanotube and fullerene products. Various methods exist for creating and harvesting various forms of solid carbon through the pyrolysis of hydrocarbons using temperature, pressure, and the presence of a catalyst to govern the resulting solid carbon morphology. For example, Kauffman, et al., (US Patent No. 2,796,331) discloses a process for making fibrous carbon of various forms from hydrocarbons in the presence of surplus hydrogen using hydrogen sulfide as a catalyst, and methods for collecting the fibrous carbon on solid surfaces. Kauffman also claims the use of coke oven gas as the hydrocarbon source.

[0008] In another study, a flame based technique is described in Vander Wal, R.L., et al., "Flame Synthesis of Single-Walled Carbon Nanotubes and Nanofibers," Seventh International Workshop on Microgravity Combustion and Chemically Reacting Systems, Aug. 2003, 73-76 (NASA Research Publication: NASA/CP—2003-212376/REV1). The technique used the introduction of a CO or CO/C₂H₂ mixture into a flame along with a catalyst to form the carbon nanotubes. The authors noted that high productivity could be achieved using flame based techniques for the production of carbon black. However, the authors noted that scaling the flame synthesis presented numerous challenges. Specifically, the total time for catalyst particle formation, inception of the carbon nanotubes, and growth of the carbon nanotubes was limited to about 100 ms.

[0009] International Patent Application Publication WO/2010/120581, by Noyes, discloses a method for the production of various morphologies of solid carbon product by reducing carbon oxides with a reducing agent in the presence of a

catalyst. The carbon oxides are typically either carbon monoxide or carbon dioxide. The reducing agent is typically either a hydrocarbon gas or hydrogen. The desired morphology of the solid carbon product may be controlled by the specific catalysts, reaction conditions, and optional additives used in the reduction reaction.

5 [0010] While all of the techniques described can be used to form carbon nanotubes, none of the processes provide a practical method for bulk or industrial scale production. Specifically, the amounts formed or the process efficiencies, or both, are low. Further, the techniques described above do not provide for the efficient removal or separation of the carbon nanotubes from impurities following
10 such a bulk or industrial scale production of the carbon nanotubes.

SUMMARY

[0011] An embodiment provides a system for removing carbon nanotubes from a continuous reactor effluent. The system includes a separation vessel configured to
15 isolate the carbon nanotubes from the continuous reactor effluent and generate a stream including gaseous components from the continuous reactor effluent.

[0012] Another embodiment provides a method for removing carbon nanotubes from a continuous reactor effluent. The method includes flowing the continuous reactor effluent through a separation vessel, separating carbon nanotubes from the
20 continuous reactor effluent in the separation vessel, and generating a stream including gaseous components from the continuous reactor effluent.

[0013] Another embodiment provides a system for creating a purified stream of carbon nanotubes from a gas flow. The system includes a separation system configured to generate a first purified stream of the carbon nanotubes and a first
25 residual stream including gaseous components from the gas flow. The system also includes a filtration system configured to generate a second purified stream of the carbon nanotubes and a second residual stream including impurities from the first purified stream of the carbon nanotubes.

DESCRIPTION OF THE DRAWINGS

[0014] The advantages of the present techniques are better understood by referring to the following detailed description and the attached drawings, in which:

[0015] **Fig. 1** is a block diagram of a reaction system that generates carbon
5 allotropes, for example, as a by-product of a carbon dioxide sequestration reaction;

[0016] **Fig. 2** is an equilibrium diagram that identifies conditions under which a solid carbon product will form;

[0017] **Fig. 3** is a simplified process flow diagram of a one reactor system for making carbon nanotubes (CNTs) from a gas feed that includes carbon dioxide and
10 methane;

[0018] **Fig. 4** is a simplified process flow diagram of a two reactor system for making CNTs from a gas feed that includes carbon dioxide and methane;

[0019] **Fig. 5** is a simplified process flow diagram of a one reactor system for making CNTs from a gas feed that includes carbon dioxide and methane, in which
15 the carbon dioxide is in excess;

[0020] **Fig. 6** is a schematic of a catalytic reaction for the formation of CNTs on a catalyst particle;

[0021] **Fig. 7** is a drawing of a fluidized bed reactor for forming CNTs;

[0022] **Fig. 8** is a schematic of a separation system in which a cyclonic separator
20 and a filter are used to isolate the CNTs from the reactor effluent stream;

[0023] **Fig. 9** is a schematic of a separation system in which a multicyclonic separator is used to isolate the CNTs from the reactor effluent stream;

[0024] **Fig. 10** is a schematic of a separation system in which an electrostatic precipitator is used to isolate the CNTs from the reactor effluent stream;

[0025] **Fig. 11** is a simplified process flow diagram of a packaging system that can package CNTs separated from a reactor effluent stream from a one reactor
25 system;

[0026] **Fig. 12** is a process flow diagram of a method for generating CNTs from a feed gas that includes methane and carbon dioxide; and

[0027] **Fig. 13** is a process flow diagram showing a method for removing CNTs from a continuous reactor effluent.

DETAILED DESCRIPTION

5 [0028] In the following detailed description section, specific embodiments of the present techniques are described. However, to the extent that the following description is specific to a particular embodiment or a particular use of the present techniques, this is intended to be for exemplary purposes only and simply provides a description of the exemplary embodiments. Accordingly, the techniques are not
10 limited to the specific embodiments described below, but rather, include all alternatives, modifications, and equivalents falling within the spirit and scope of the appended claims.

[0029] At the outset, for ease of reference, certain terms used in this application and their meanings as used in this context are set forth. To the extent a term used
15 herein is not defined below, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Further, the present techniques are not limited by the usage of the terms shown below, as all equivalents, synonyms, new developments, and terms or techniques that serve the same or a similar purpose are considered to be within the
20 scope of the present claims.

[0030] Carbon fibers, nanofibers, and nanotubes are allotropes of carbon that have a cylindrical structure, which can be in the nanometer range. Carbon nanofibers and nanotubes are members of the fullerene structural family, which includes the spherical carbon balls termed "Buckminster fullerene." The walls of the
25 carbon nanotubes are formed from sheets of carbon in a graphene structure. As used herein, nanotubes may include single wall nanotubes and multiple wall nanotubes of any length. The terms "carbon allotropes" and "carbon nanotubes" as used herein, include carbon fibers, carbon nanofibers, and other carbon nanostructures.

[0031] A “compressor” is a device for compressing a working gas, including gas-vapor mixtures or exhaust gases, and includes pumps, compressor turbines, reciprocating compressors, piston compressors, rotary vane or screw compressors, and devices and combinations capable of compressing a working gas. In some
5 embodiments, a particular type of compressor, such as a compressor turbine, may be preferred. A piston compressor may be used herein to include a screw compressor, rotary vane compressor, and the like.

[0032] A “hydrocarbon” is an organic compound that primarily includes the elements hydrogen and carbon, although nitrogen, sulfur, oxygen, metals, or any
10 number of other elements may be present in small amounts. As used herein, hydrocarbons generally refer to components found in natural gas, oil, or chemical processing facilities.

[0033] As used herein, the term “natural gas” refers to a multi-component gas obtained from a crude oil well or from a subterranean gas-bearing formation. The
15 composition and pressure of natural gas can vary significantly. A typical natural gas stream contains methane (CH_4) as a major component, i.e., greater than 50 mol % of the natural gas stream is methane. The natural gas stream can also contain ethane (C_2H_6), higher molecular weight hydrocarbons (e.g., C_3 - C_{20} hydrocarbons), one or more acid gases (e.g., carbon dioxide or hydrogen sulfide), or any combination
20 thereof. The natural gas can also contain minor amounts of contaminants such as water, nitrogen, iron sulfide, wax, crude oil, or any combination thereof. The natural gas stream may be substantially purified prior to use in embodiments, so as to remove compounds that may act as poisons.

[0034] A “low-BTU natural gas” is a gas that includes a substantial proportion of
25 CO_2 as harvested from a reservoir. For example, a low BTU natural gas may include 10 mol % or higher CO_2 in addition to hydrocarbons and other components. In some cases, the low BTU natural gas may include mostly CO_2 .

[0035] As used herein, a “plant” is an ensemble of physical equipment in which chemical or energy products are processed or transported. In its broadest sense,
30 the term plant is applied to any equipment that may be used to produce energy or

form a chemical product. Examples of facilities include polymerization plants, carbon black plants, natural gas plants, and power plants.

[0036] Overview

[0037] Embodiments described herein provide systems and methods for
5 separating carbon nanotubes (CNTs) entrained in an effluent stream from a reactor. The removal allows for the isolation of the carbon nanotubes for packaging.

[0038] The carbon nanotubes may be made using feedstocks that can include nearly stoichiometric mixtures of carbon dioxide and methane, among others. In some embodiments, the feedstocks are higher in CH₄, while in other embodiments,
10 the feedstocks are higher in CO₂. Other feedstocks may be used, including mixtures of any number of compounds having C, H, and O, such as H₂, CO, CO₂, and other hydrocarbons. The process is conducted under high temperature and pressure conditions using a Bosch-like reaction, as discussed with respect to **Fig. 2**.

[0039] The process may be slightly exothermic, energy neutral, or slightly
15 endothermic, depending upon the level of reforming relative to carbon formation taking place in the specific design. Accordingly, at least a portion of the heat from the effluent can be recovered and used to heat the feed gases, providing a portion of the heat used by the process during continuous operations. As a high pressure process is used, an ambient temperature heat exchanger is sufficient for the removal
20 of water vapor from the product stream, without using cryogenic coolers. After separation of the product and water formed during the reaction, a gas fractionation system is used to separate any remaining amounts of the limiting reagent from a waste gas mixture and recycle the limiting reagent to the process. In addition, fuel for the process can be supplied using the effluent stream either prior to or after gas
25 fractionation.

[0040] As used herein, an ambient temperature heat exchanger can include water chillers, air coolers, or any other cooling system that exchanges heat with a source that is at substantially ambient temperature. It can be understood that ambient temperature is substantially the temperature of the outside air at the location of the
30 facility, e.g., ranging from about -40 °C to about +40 °C, depending on the location of

the facility. Further, different types of ambient temperature heat exchangers may be used depending on current ambient temperature. For example, a facility that uses water chillers in a summer season may use air coolers in a winter season. It can be understood that an appropriate type of heat exchanger may be used at any point
5 herein that describes the use of an ambient temperature heat exchanger. The ambient temperature heat exchangers may vary in type across the plant depending on the amount of cooling needed.

[0041] The present process can use various feedstocks, including, for example, carbon, hydrogen, and oxygen. For example, feedstocks can include a carbon
10 oxide, e.g., carbon dioxide (CO₂) or carbon monoxide (CO), and a reducing agent, e.g., methane (CH₄) or other hydrocarbons, hydrogen (H₂), or combinations thereof. The reducing agent may include other hydrocarbon gases, hydrogen (H₂), or mixtures thereof. A hydrocarbon gas can act as both an additional carbon source and as the reducing agent for the carbon oxides. Other gases, such as syngas, are
15 created as intermediate compounds in the process or may be contained in the feed. These gases can also be used as the reducing agent. Syngas, or "synthetic gas," includes carbon monoxide (CO) and hydrogen (H₂) and, thus, includes both the carbon oxide and the reducing gas in a single mixture. Other compounds that include both carbon and oxygen may be used instead of, or in addition to, the
20 feedstocks above. In some embodiments, any feedstock with a C, H, and O makeup that falls within the prescribed area in **Fig. 2** can be used to make these products.

[0042] Carbon oxides, particularly carbon dioxide, are abundant gases that may be extracted from exhaust gases, low-BTU well gas, and from some process off-gases. Although carbon dioxide may also be extracted from the air, other sources
25 often have much higher concentrations and are typically more economical sources from which to harvest the carbon dioxide. Further, carbon dioxide is available as a by-product of power generation. The use of CO₂ from these sources may lower the emission of carbon dioxide by converting a portion of the CO₂ into carbon products.

[0043] According to embodiments disclosed herein, various separation
30 techniques may be used to separate carbon nanotubes from a residual gas stream,

e.g., a stream including gaseous components and other impurities, from a continuous reactor effluent. Such separation techniques include, for example, cyclonic separation, magnetic separation, density based separation, electrostatic separation, or gravity separation techniques, among others. For example, in some
5 embodiments, a multicyclonic separator may be used to separate a purified stream of CNTs from a residual stream of impurities. In other embodiments, a filtration system, such as a sintered ceramic or sintered metal filtration system, may be used to separate the purified stream of CNTs from the residual stream of impurities.

[0044] As used herein, an industrial scale process may provide large quantities of
10 carbon allotropes in short periods of time. For example, the techniques used herein may provide carbon allotropes in quantities greater than about 0.5 Kg / hr, greater than about 1 Kg / hr, greater than about 2 Kg / hr, greater than about 5 Kg / hr, greater than about 10 Kg / hr, greater than about 100 Kg / hr, or greater than 1000 Kg / hr. The amounts produced depend on the scale of the equipment and the
15 catalysts chosen.

[0045] **Fig. 1** is a block diagram of a reaction system **100** that generates carbon allotropes, for example, as a by-product of a carbon dioxide sequestration reaction. The reaction system **100** is provided with a feed gas **102**, which can be a mixture of CO₂ and CH₄. In some embodiments, the reaction may allow for sequestration of
20 CO₂ from exhaust streams of power plants and the like. In other embodiments, the CH₄ is at a higher concentration, for example, in a gas stream from a natural gas field. Other components may be present in the feed gas **102**, such as C₂H₆, C₂H₄, and the like. In one embodiment, the feed gas **102** has been treated to remove these components, for example, for sale as product streams.

[0046] The feed gas **102** is passed through a heat exchanger **104** to form a heated feed gas **106**. During continuous operation, a portion of the heating is provided using heat **108** recovered from the reaction. The remaining heat for the reaction may be provided by an auxiliary heater, as described below. During start-up, the auxiliary heater is used to provide the total heat to bring the feed to the
25 appropriate reaction temperature, e.g., about 500 °C (about 930 °F). In one
30

embodiment, the feed is heated to between about 500 °C (about 932 °F) to about 550 °C (about 1022 °F). In another embodiment, the feed is heated to between about 700 °C (about 1292 °F) to about 750 °C (about 1382 °F). In another embodiment, the feed is heated to between about 800 °C (about 1472 °F) to about 850 °C (about 1562 °F). The heated feed gas **108** is fed to a reactor **110**.

[0047] In the reactor **110**, a catalyst reacts with a portion of the heated feed gas **106** to form carbon nanotubes (CNTs) **112**, and other carbon allotropes, using Bosch-like reactions. As described in more detail below, the reactor **110** can be a fluidized bed reactor that uses any number of different catalysts, including, for example, metal shot, supported catalysts, and the like. The CNTs **112** are separated from the reactor effluent **114**, leaving a waste gas stream **116** containing excess reagents and water vapor. At least a portion of the heat from the reactor effluent **114** is used to form the heated feed gas **106** prior to the reactor effluent **114** entering the chiller as the waste gas stream **116**.

[0048] The separation of the CNTs **112** from the reactor effluent **114** may be accomplished using a separation system **118**. In various embodiments, the separation system **118** may be directly coupled to the reactor **110**, as shown in **Fig. 1**. The reactor effluent **114** may be a continuous reactor effluent containing the CNTs **112**, as well as gaseous components and excess reagent. It is desirable to efficiently isolate the CNTs **112** from the reactor effluent **114** in order to increase the degree of purity of the final carbon nanotube product and to lower the amount of CNTs that are carried over into the waste streams.

[0049] In some embodiments, an initial separation process may be performed within the separation system **118** to separate catalyst particles **120** from the reactor effluent **114**. For example, a magnetic separation vessel or a cyclonic separation vessel located within the separation system **118** may be used to remove the catalyst particles **120** from the reactor effluent **114**. The catalyst particles **120** may then be returned to the reactor **110**, as indicated in **Fig. 1**. It is often useful to recycle such catalyst particles **120** to the reactor **110** to be reused for the creation of the CNTs **112** within the reactor **110** and to lower the amount of metal in the final product.

[0050] In various embodiments, the separation system **118** may also be configured to isolate the CNTs **112** from the reactor effluent **114** and generate the waste gas stream **116**. The waste gas stream **116** may include gaseous components, such as excess reagents, small amounts of CNTs **112**, and other
5 impurities. The separation of the CNTs **112** from the reactor effluent **114** may be accomplished through a variety of techniques. For example, in some embodiments, the separation system **118** may be configured to perform a gravity separation process. The gravity separation process may be implemented using a cyclonic separator, multicyclonic separator, or drift separator, among others. In some
10 embodiments, the separation system **118** may be configured to perform an electrostatic separation process using, for example, an electrostatic precipitator or other electrostatic separation unit. Further, in some embodiments, the separation system **118** may be configured to perform a magnetic separation process using, for example, paramagnetic catalysts.

[0051] In various embodiments, the separation system **118** may contain a filter that is configured to aid in the separation of the CNTs **112** from the reactor effluent **114**. The filter may be a sintered ceramic filter, a sintered metal filter, a fabric bag filter, or a fluidized bed filter, among others. In addition, the filter may be configured to perform a self-cleaning procedure to remove any remaining CNTs **112** or other
15 residual particles. Further, in some embodiments, the separation system **118** may contain any number of additional components for removing the CNTs **112** from the reactor effluent **114**. Once the CNTs **112** have been sufficiently purified, they may be provided to the market.

[0052] The waste gas stream **116** is passed through an ambient temperature heat
25 exchanger, such as water chiller **122**, which condenses out the water **124**. The resulting dry waste gas stream **126** can be used as a feed stream for a gas fractionation system **128**, or may be directly recycled in part. It can be understood that a dry waste gas stream, as used herein, has the bulk of the water removed, but may still have small amounts of water vapor. For example, the dew point of a dry
30 waste gas stream may be greater than about -5 °C, greater than about 0 °C, greater

than about 5 °C, greater than about 10 °C, greater than about 20 °C, or higher. A dryer may be used to lower the dewpoint, for example, to about -50 °C, about -70 °C, or lower, as part of the gas fractionation system **128**.

[0053] The gas fractionation system **128** removes a portion of the reagent having the lower concentration in the feed gas **102** and recycles it to the process, for example, by blending a recycle stream **130** with the feed gas **102**. The higher concentration gas in the feed gas **102** can be disposed of as excess feed **132**, for example, by sales to downstream users. As an example, if CO₂ is the highest concentration gas in a blend with CH₄, the gas fractionation system **128** can be used to remove CH₄ remaining in the waste gas stream, and send it back into the process as recycle stream **130**. The process functions as an equilibrium reaction between the reagents and solid carbon, as discussed further with respect to **Fig. 2**. The gas fractionation system **128** may not be needed when the CH₄ is in excess, as much of the CO₂ may be consumed in the reaction. Thus, the excess feed **132** that contains the CH₄, and which may also contain H₂, CO, and other gases, may be used to generate power in a power plant without further purification or gas separation. Further, in that circumstance, a portion of the dry waste gas stream **126** may be recycled to the process without further treatment.

[0054] **Fig. 2** is an equilibrium diagram that identifies conditions under which a solid carbon product will form. This diagram is a triangular diagram **200** with the elements, C **202**, H **204**, and O **206**, at the apexes of the triangle. As one moves from any location towards an apex the molar ratio of the element, C **202**, H **204**, and O **206**, increases. In this way all of the possible compositions of the three elements can be mapped onto the triangular diagram **200**.

[0055] Any chemical compound, or mixture, with any two or all these three elements can be mapped onto the triangular diagram **200** as indicated by the exemplary points marked. Some of the chemical compounds include hydrocarbons such as alkanes, alkenes, and alkynes, as well as many other types of hydrocarbons. The hydrocarbons are located on the C-H edge **208** connecting C **202** and H **204**. Chemical compounds that include only the elements C **202** and O

206, including carbon monoxide (CO) and carbon dioxide (CO₂), occur along the C-O edge **210** connecting C **202** and O **206**. Chemical compounds that include only the elements H **204** and O **206**, such as water (H₂O), occur along the H-O edge **212** connecting H **204** and O **206**.

5 [0056] In the central region of the triangular diagram **200** are chemical compounds and mixtures that have all three elements, C **202**, H **204**, and O **206**. For example, these chemical compounds may include a very large number of individual components, such as alcohols, aldehydes, ethers, and materials with more complex structures, such as carbohydrates. Further, mixtures of compounds such
10 as hydrogen, carbon oxides, and hydrocarbons may also be present.

[0057] Some of the first experiments to form fullerenes, C₆₀ and C₇₀, as well as carbon nanotubes (CNTs) were performed by laser ablation of a carbon electrode, capturing the carbon material in a mass spectrometer. The curves **214** shown in **Fig. 2** show the limit of carbon production at various temperatures. These curves
15 **214** were determined by performing a stoichiometrically constrained Gibbs minimization, which minimizes the Gibbs free energy of the resulting compounds based on the constraint that the amount of carbon, oxygen, and hydrogen are to be the same both before and after the reaction. The point where solid carbon formation occurs for the first time was noted as the composition was moved from a first
20 composition point to a second composition point on the triangular diagram **200**.

[0058] In thermodynamic terms, the curves **214** identify the points where the activity of carbon is about 1.0. Above a carbon activity of about 1.0, carbon solid forms in the center region, while below the carbon activity of about 1.0, no solid carbon forms. The triangle diagram **200** is useful for identifying the conditions where
25 carbon allotropes, such as carbon nanotubes (CNTs) can possibly be produced, as well as determining compounds and mixtures that can be used for their production.

[0059] At the temperatures indicated in **Fig. 2**, most hydrocarbons, and other organic compounds, undergo thermal decomposition to produce small, thermodynamically stable, gas molecules, such as CO, CO₂, CH₄, H₂O, H₂, and the
30 like. Under certain reaction conditions, these small gas molecules can react to

produce carbon allotropes. In some cases, the carbon allotropes will be in the form of CNTs. Both single walled and multi-walled CNTs of various dimensions and chiralities can be made in these ways.

[0060] Reaction Pathways for the Formation of Carbon Allotropes

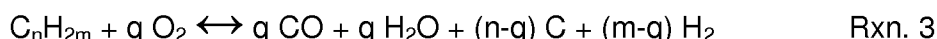
5 [0061] Hydrocarbons undergo thermal decomposition in two ways, depending upon the concentration of oxygen. Without oxygen being present, large hydrocarbon molecules will thermally decompose into smaller hydrocarbons, such as methane, ethane, propane, and hydrogen. These small hydrocarbons will further decompose to carbon and more hydrogen, giving an overall reaction as shown in Rxn. 1. This
10 reaction, termed a pyrolysis reaction, occurs along the C-H edge **208**.



A representative case is the thermal decomposition of methane, shown in Rxn. 2.



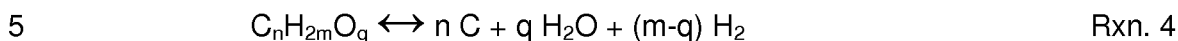
[0062] In the presence of a low amount of oxygen, hydrocarbons will react to form
15 carbon monoxide and carbon dioxide and water as well as carbon allotropes and hydrogen according to the reaction shown in Rxn. 3. This reaction is termed the Bosch reaction, and occurs in the center region of the triangular diagram **200**.



The ratio of CO to H₂O after reaction may differ depending upon the temperature of
20 the system. Further, depending upon the amount of oxygen there may be some carbon dioxide in the product gases. Any carbon monoxide or carbon dioxide produced may react to form carbon allotropes at the high temperature conditions. Higher concentrations of O₂ typically results in higher temperatures, due to combustion, resulting in the production of more CO and CO₂ and less solid carbon
25 and hydrogen. Thus, the reaction system must restrict the amount of oxygen present in the system in order to produce larger amounts of carbon allotropes.

[0063] Organic compounds that include small amounts of oxygen may also be useful in the production of carbon allotropes. These compounds thermally

decompose to form small, thermodynamically stable, gas molecules which can further react on a catalyst surface to produce carbon allotropes and water according to the overall reaction shown in Rxn. 4, which is another example of the Bosch reaction.



[0064] Any carbon monoxide or carbon dioxide produced has a tendency to react to carbon at these high-temperature conditions, adding to the overall productivity. These reactions form the simplest embodiments of the Bosch reaction, shown in Rxn. 5.



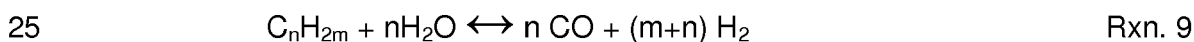
The Bosch reaction can be mechanistically written as two separate reactions in which CO is produced as an intermediate, as shown in Rxns. 6 and 7.

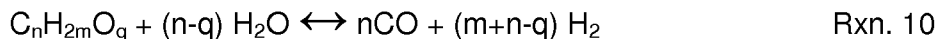


15 The first, Rxn. 6, is fast and tends toward equilibrium. The second, Rxn. 7, is slow. Another reaction that can produce carbon allotropes is the Boudouard reaction that is shown in Rxn. 8. The Boudouard reaction takes place on the C-O edge **210**, and produces carbon allotropes and carbon dioxide from carbon monoxide.



20 [0065] In addition to forming small molecules directly in the reactor, a number of other approaches may be used to provide the reactants to form the carbon allotropes. For example, steam reforming of hydrocarbons and other organic chemicals may be used. In these reactions, shown in Rxns. 9 and 10, a mixture of CO and hydrogen, called syngas, is formed.





At the reaction temperatures shown in the triangular diagram **200**, the syngas forms carbon allotropes via the second step of the Bosch reaction mechanism, shown in Rxn. 7.

5 [0066] As is apparent in the reactions shown above, there is a multitude of starting points for the production of carbon allotropes, such as CNTs. However, the reactions can be simplified by focusing on the conversion of the feedstock compounds into a mixture of small, thermodynamically stable, gases. These gases can then react to form carbon allotropes in the presence of a catalyst. This
10 simplification can be performed by noting that a given hydrocarbon reacting with oxygen or with steam will be converted to carbon monoxide, carbon dioxide, water vapor, and hydrogen. Similarly, a given oxygenate reacting with itself, or with oxygen or steam, will also be converted to carbon monoxide, carbon dioxide, water vapor, and hydrogen. The ultimate mixture of small thermodynamically stable gases
15 can be determined by performing equilibrium calculations on the reactions described above.

[0067] The gas mixture can then be converted to carbon allotropes in the Boudouard Reaction shown in Rxn. 8, step two of the Bosch reaction shown in Rxn. 7, the methane pyrolysis reaction shown in Rxn. 2, or some combinations of
20 these. As all of these reactions produce carbon allotropes, they may be used to predict the carbon activity as a function of the composition of carbon monoxide, carbon dioxide, hydrogen, water vapor, methane, or the like, which are produced by some previous thermal decomposition reaction.

[0068] Oxidation Poisoning of Metal Catalysts

25 [0069] Another aspect of the catalytic reaction to produce carbon allotropes is that certain gas compositions and temperatures will oxidize the metal catalyst used in the reaction, rendering it ineffective for further catalytic reaction, as shown in Rxn. 11. The point where oxygen causes a metal or alloy to oxidize depends upon

its properties. For elemental metals, this is determined by the Gibbs free energy of formation of the oxide.



[0070] If a catalyst includes iron, there are various oxides that may be formed.

- 5 The most common include Wüstite (FeO), magnetite (Fe₃O₄), and hematite (Fe₂O₃). Wüstite is thermodynamically favored at the temperatures and pressures shown in **Fig. 2** and forms by the reaction shown in Rxn. 12.



An equilibrium constant, K_{FeO} , for Rxn 12 can be determined by the formula shown in

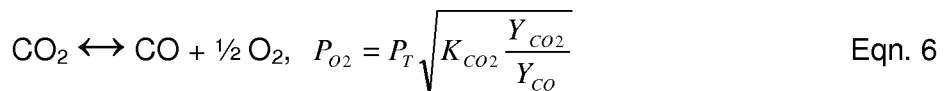
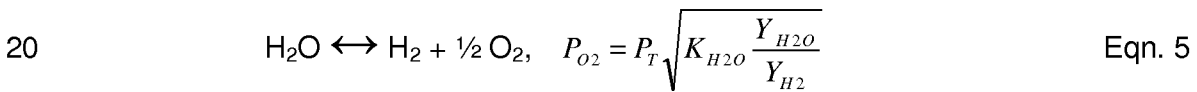
10 Eqn. 4.

$$K_{FeO} = \exp [-\Delta G_{FeO}/(R_g T)] = [P_{O_2}/P_T]^{-1/2} \quad \text{Eqn. 4}$$

In Eqn. 4, ΔG_{FeO} is the Gibbs free energy of iron oxidation to Wüstite which is a function of temperature, R_g is the gas constant, T is the absolute temperature, P_{O_2} is the partial pressure of oxygen (O₂), and P_T is the total pressure of the system. The

15 ratio, P_{O_2}/P_T , is simply the mole fraction of O₂ in the system. Using this equation, the partial pressure of oxygen that will initiate the oxidation of iron at any temperature can be identified.

[0071] The partial pressure of oxygen can be obtained from one of the fast reaction equilibria presented in Eqns. 5 and 6.



In these equilibria calculations, K_i is the equilibrium constant, a function of temperature, for the decomposition of gas i . As shown by Eqns. 5 and 6, the partial pressure of oxygen is controlled by either the mole fraction ratio of water vapor to

25 hydrogen or the mole fraction ratio of carbon dioxide to carbon monoxide at a given temperature.

[0072] As shown in Eqns. 1-6, the mole fraction ratios are important for determining both the partial pressure of oxygen and defining the carbon activity for the Boudouard and Bosch reaction mechanisms. For example, the mole fraction ratio sets both the carbon activity and the partial pressure of oxygen, so that there
5 will be a given activity of carbon that will initiate the oxidation of the metal catalyst.

[0073] As the pyrolysis reactions are endothermic, their zone of influence is near the H **204** apex of the triangle diagram **200**, where the temperature lines curve, inverting the temperature sequence as the amount of carbon in the system increases. As a result, a zone **216** near the C-H edge **208** may be delineated in the
10 triangle near the H apex, where pyrolysis reactions dominate over Bosch reactions. As the transition point changes as the temperature of the system changes, two lines **218** and **220** can be used to indicate the edge of the zone **216**, depending on the temperature. The first line **218** delineates the zone **216** at about 1173.45 K (about 900 °C), while the second line **220** delineates the zone **216** at about 973.15 K (about
15 700 °C). The pyrolysis reactions dominate over the Bosch reactions in the zone between either of the lines **218** or **220** and the C-H edge **208**.

[0074] Further, from the Ac produced by both the Bosch second step and the Boudouard reactions, a zone near the C-O edge **210** can be identified at which there is an equal probability for the first solid carbon allotropes to be produced by either
20 reaction, based on the thermodynamics. One edge of this zone can be delineated by a first line **222** in the triangle diagram **200**. Further, as discussed above, there is a point at which the second step of the Bosch reaction generates sufficient water to cause the partial pressure of oxygen to be sufficiently high that the iron catalyst will oxidize to Wüstite. At this point **224** the first line **222** becomes dotted and a second
25 line **226**, at a fixed hydrogen (H) content of about 0.14 for FeO, limits the Boudouard zone at about 1 atm system pressure. The Boudouard zone **228** dominates over the Bosch reaction at reaction conditions above and to the right of the first line **222** and to the right of the second line **222** (FeO oxidation).

[0075] Conclusion

[0076] The calculations discussed with respect to **Fig. 2** identify carbon activity as the driving force for the production of carbon allotropes, such as CNTs. Thus, in embodiments, various reaction mixtures in the C-H-O system can be reduced to a prediction of the carbon activity using three carbon forming reactions that are applicable on the C-H edge **208**, C-O edge **210**, and the central portion of the triangular diagram of the C-H-O system. Carbon activities larger than about 1.0 produces carbon by each of the three carbon forming reactions. In some cases the carbon activity is a predictor of the transformation of iron to Wüstite, FeO. In these cases, the carbon activity where iron oxidizes will limit the carbon activity range where carbon can form to values larger than about 1.0. In the case of the Bosch second step reaction with equimolar CO:H₂ feed at about 973.15 K (about 700 °C) the carbon activity is limited to values larger than 35 for example.

[0077] Further, the calculations show clearly delineated zones where pyrolysis (zone **216**) and Boudouard reactions (zone **228**) dominate on the C-H edge **208** and C-O edge **210**, respectively, of the triangle diagram **200**. This also shows that experimental conditions in the central part of the triangular diagram of the C-H-O system define a Bosch reaction region **230** that provides the largest reactor conversion resulting in faster production and higher yields than reactions on the C-H edge **208** or C-O edge **210** of the triangular diagram **200**. In this region, the concentration of the carbon is set by the A_c , and is greater than about 10 %. Further, the oxygen content is greater than about 10 %, and the hydrogen concentration is greater than about 20 %.

[0078] Reaction Systems

[0079] **Fig. 3** is a simplified process flow diagram of a one reactor system **300** for making carbon nanotubes (CNTs) from a gas feed that includes carbon dioxide and methane. As shown, the one reactor system **300** can be used for feed gas **302** that is higher in CO₂ or higher in CH₄. More specific reactor systems are discussed with respect to Figs. 5 and 6. In the one reactor system **300**, the feed gas **302** is

combined with a recycle gas **304** that has an enhanced concentration of the lesser gas. This may be done using a static mixer **306**.

[0080] The combined gas stream **308** is passed through a heat exchanger **310** or set of heat exchangers **310** in series to be heated by a reactor effluent stream. The temperature can be raised from a near ambient temperature, as defined herein, to an appropriate reaction temperature, such as about 500 °C (930 °F), about 600 °C (about 1112 °F), about 700 °C (about 1292 °F), about 800 °C (about 1472 °F), or about 900 °C (about 1652 °F) for the heated gas stream **312**. This temperature may be sufficient for maintaining the reaction during continuous operations. However, part of the heat may be provided by a package heater **314**, which may be especially useful for adding heat to bring the reactants up to temperature during start-up. The hot gas stream **316** is then introduced into a fluidized bed reactor **318**. A general fluidized bed reactor that may be used in embodiments is discussed with respect to **Fig. 7**. In the fluidized bed reactor **318**, CNTs are formed on catalyst particles. The catalyst particles and reactions are also discussed with respect to **Fig. 6**.

[0081] The CNTs are carried from the first fluidized bed reactor **318** in a reactor effluent stream **320**. The reactor effluent stream **320** may be at an elevated temperature, for example, about 600 °C (about 1112 °F), about 700 °C (about 1292 °F), about 800 °C (about 1472 °F), or about 900 °C (about 1652 °F), and may be cooled by exchanging heat with the combined gas stream **308**, for example, providing some or all of the heat used to heat the reactants. Either prior to or after cooling, the reactor effluent stream **320** is passed through a separation system **322** to isolate the CNTs **324**.

[0082] In some embodiments, the separation system **322** may contain a catalyst separation device, such as a cyclonic separation device or a magnetic separation device, for removing excess catalysts, from the reactor effluent stream **320**. The removed catalysts may then be returned to the fluidized bed reactor **318**.

[0083] The separation system **322** may also contain one or more separation devices configured to isolate the CNTs **324** from the reactor effluent stream **320** and generate a waste gas stream **326** including gaseous components from the reactor

effluent stream **320**. For example, the waste gas stream **326** may include waste gas from the fluidized bed reactor **318**, as well as metal residues and other impurities. The CNTs **324** that are isolated from the reactor effluent stream **320** may be sent to the market.

5 **[0084]** In various embodiments, the separation system **322** may include a gravity separation vessel, such as a drift separator, or a separator based on centripetal force, such as a cyclonic separator, or a multicyclonic separator, among others. The separation system **322** may also include a magnetic separation vessel or an electrostatic separation vessel, such as an electrostatic precipitator. Further, the separation system **322** may contain any type of separation device that is capable of separating the CNTs **324** from the waste gas stream **326**.

[0085] In some embodiments, the separation system **322** may include a filter device for aiding in the purification of the CNTs **324**. This is discussed further with respect to **Fig. 8**.

15 **[0086]** The isolation of the CNTs within the separation system may result in the generation of the waste gas stream **326**, as discussed above. The waste gas stream **326** can be used to provide heat to the combined gas stream **308** in the heat exchanger **310**. The carbon may also be removed within the separation system **322** at lower temperatures than the waste gas stream **326**.

20 **[0087]** After providing heat to the combined gas stream **308**, the cooled waste stream **328** is passed through an ambient temperature heat exchanger **330** and then fed to a separation vessel **332**. Water **334** settles in the separation vessel **332** and is removed from the bottom. The resulting gas stream **336** may be significantly cooler, for example, at about 30 °C, about 38 °C (about 100 °F), or about 40 °C and at a pressure of about 2500, kilopascals (kPa), about 3000 kPa, about 3720 kPa (about 240 psia), or about 4000 kPa. In one embodiment, the gas is then dried to a low dew point in a drier (not shown). The stream enters a compressor **338** that increases the pressure of the gas stream **336**, for example, to about 5000 kPa, about 6000 kPa, about 7000 kPa, about 7,240 kPa (about 1050 psia), or about 8000 kPa, forming a high pressure stream **340** which is passed through another ambient

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temperature heat exchanger **342**. From the ambient temperature heat exchanger **342**, the high pressure stream **340** is fed to a separation vessel **344** for removal of any remaining water **334**, for example, if a drier has not been used.

[0088] In embodiments in which the CO₂ is in excess in the feed gas **302**, the dried gas stream **346** is then sent to a gas fractionation system **348**, which separates the excess feed **350** from the recycle gas **304**. In reaction systems **300** based on a proportionate excess of CO₂, the excess feed **350** may primarily include CO₂, and the recycle gas **304** may primarily include CH₄. In reaction systems **300** based on a proportionate excess of CH₄, the excess feed **350** will not have a substantial CO₂ content, and a portion may be recycled without further purification. In some embodiments, a portion of the excess feed **350**, the recycle gas **304**, or both may be tapped to provide a fuel gas stream, a purge gas stream, or both for use in the plant.

[0089] The reaction conditions used can cause significant degradation of metal surfaces, as indicated by choice of the catalyst itself, which may include carbon or stainless steel in various forms. Accordingly, the process may be designed to decrease the amount of metal exposed to the process conditions, as discussed further with respect to the following figures.

[0090] **Fig. 4** is a simplified process flow diagram of a two reactor system **400** for making CNTs from a gas feed that includes carbon dioxide and methane. Like numbered items are as discussed with respect to **Fig. 3**. In the two reactor system **400**, the resulting waste gas stream **402** is used to provide heat in a heat exchanger **404**. The carbon may also be removed in secondary separation devices at lower temperatures than the waste gas stream **402**. This is particularly easy to do where multiple heat exchangers in parallel may be used to cool the waste gas stream **402** while heating the feed gas to the next reactor in a sequence. Normally, all of the carbon solids will be removed by separation device(s) prior to the condensation of any of the water vapor present in the waste gas stream **402**.

[0091] The cooled waste gas stream **406** is then passed through an ambient temperature heat exchanger **408**, which further cools the cooled waste gas stream **406** and results in the bulk of the water formed condensing as a liquid, which is then

fed to a separation vessel **410**. Water **334** is removed from the separation vessel, and a reactant stream **412** exits the top of the separation vessel **410** at about 30 °C, about 38 °C (about 100 °F), about 40 °C, or about 50 °C.

[0092] The reactant stream **412** passes through the heat exchanger **404** and is
5 heated by waste heat from the waste gas stream **402**. The heated stream **414** is the fed to a second fluidized bed reactor **416** in which additional CNTs **324** are formed. However, the heated stream **414** may not be at a sufficiently high temperature, e.g., greater than about 850 °C (about 1562 °F), to form CNTs **324** in the second fluidized bed reactor **416**. To increase the temperature of the heated stream **414**, a second
10 package heater **418** may be used. The second package heater **418** may be a separate heating zone in the first package heater **314**. In some embodiments, a second reactor effluent stream **420** is used to provide heat to the heated stream **414**. The second reactor effluent stream **420** is then fed to a second separation system **422** to isolate the CNTs **324** from the second reactor effluent stream **420**. In various
15 embodiments, the second separation system **422** may include any number of separation devices, such as those discussed with respect to the separation system **322**. The resulting waste gas stream **424** is used to provide heat to the combined gas stream **308** as it passes through the heat exchanger **310**.

[0093] Although only two fluidized bed reactors **318** and **416** are shown in this
20 embodiment, the reaction system **400** may contain more reactors if desired. The determination of the number of reactors can be based on the concentration of the feedstocks and the desired remaining amount of each feedstock. In some circumstances, three, four, or more reactors may be used in sequence, in which an effluent stream from each reactor provides heat to a feed gas for the next reactor in
25 the sequence. Further, the reactors do not have to be fluidized bed reactors, as other configurations may be used in other embodiments. For example, a fixed bed reactor, a tubular reactor, a continuous feed reactor, or any number of other configurations may be used. As noted, in embodiments in which the CH₄ is in excess, the gas fractionation system **348** can be replaced with a manifold that can
30 divide the dried gas stream **346** into the excess feed **350** and a recycle gas **304**.

[0094] **Fig. 5** is a simplified process flow diagram of a one reactor system **500** for making CNTs from a gas feed that includes carbon dioxide and methane, in which the carbon dioxide is in excess. In **Fig. 5**, like number items are as described with respect to **Fig. 3**. As for **Fig. 3**, the feed gas **302** passes through a static mixer **306** where it is combined with a recycle gas **304**, which is high in methane. The combined gas stream **308** is passed through a heat exchanger **310**, for example, including multiple shell and tube heat exchangers **502**. The main difference between the more detailed process flow diagram of **Fig. 5** and that of **Fig. 3** is the use of heat exchangers to cool the reactor effluent stream **320** prior to separating the CNTs from the reactor effluent stream **320**.

[0095] In this embodiment, the heated gas stream **312** is raised to a temperature of about 300 °C, about 400 °C, about 427 °C (about 800 °F), or about 500 °C in the heat exchanger **310** prior to flowing through a second heat exchanger **504**. In the second heat exchanger **504**, the heated gas stream **312** flows through a first ceramic block heat exchanger **506**, as indicated by arrow **508**. Heat stored in the first ceramic block heat exchanger **506** is exchanged to the heated gas stream **312** and may increase the temperature to between about 500 °C (about 932 °F) and to about 550 °C (about 1022 °F). In another embodiment, the feed is heated to between about 700 °C (about 1292 °F) to about 750 °C (about 1382 °F). In another embodiment, the feed is heated to between about 800 °C (about 1472 °F) to about 850 °C (about 1562 °F).

[0096] While the first ceramic block heat exchanger **506** is used to heat the heated gas stream **312**, a second ceramic block heater **510** is used to cool the reactor effluent stream **320** by flowing this stream through the second ceramic block heater **510**, as indicated by arrows **512**. When the second ceramic block heat exchanger **510** reaches a selected temperature, or the first ceramic block heat exchanger **506** drops to a selected temperature, the positions of the inlet valves **514** and outlet valves **516** are changed. In other words, open valves are closed and closed valves are opened. The change in the positions of the valves changes which ceramic block heat exchanger **506** or **510** is being heated by the flow from the

reactor **318** and which ceramic block heat exchanger **506** or **510** is used to heat the heated gas stream **312**.

[0097] The heat may not be sufficient to increase the temperature sufficiently for reaction. Thus, as described with respect to **Fig. 3**, a package heater **314** can be
5 used to further boost the temperature of the heated gas stream **312**, forming the hot gas stream **316**, which can be fed to the fluidized bed reactor **318**. CNTs **324** are formed in the fluidized bed reactor **318**, and carried out in the reactor effluent stream **320**.

[0098] After flowing through the second ceramic block heater **510**, the reactor
10 effluent **320** is flowed to a separation system **518**, which is used to remove the CNTs **324** from the reactor effluent **320**. In this embodiment, the separation system **518** for the CNTs **324** includes a cyclonic separator **520**, a lock hopper **522**, and a filter **524**. However, the separation system **518** may also include any number of other separation devices, such as those discussed with respect to the separation system
15 **322**, arranged in any type of configuration. After the majority of the CNTs are removed by the cyclonic separator **520** and deposited into the lock hopper **522**, the filter **524** is used to remove remaining CNTs **324** from the waste gas stream **526**. This may help to prevent plugging, or other problems, caused by residual CNTs **324** in the waste gas stream **526**. The filter **524** can include bag filters, sintered metal
20 filters, and sintered ceramic filters, among other types. From the CNT separation systems **518**, the CNTs **324** may be directed to a packaging system, as discussed in further detail with respect to **Fig. 12**. After the filter **524**, the waste gas stream **526** is flowed through the heat exchanger **310** before flowing to the ambient temperature heat exchanger **330** and then fed to a separation vessel **332** for separation of the
25 water. After flowing through the separation vessel **332**, the flow is as described with respect to **Fig. 3**.

[0099] In this embodiment, two extra streams may be provided from the separated streams out of the gas fractionation system **348**. A fuel gas stream **528** may be taken from the recycle gas **304** to meet internal fuel demands and could, if
30 warranted, be sent to a power plant. A purge gas stream **530** may be taken from the

CO₂ outlet stream, which can be used to purge various pieces of equipment, such as the filter **524** or cyclone **520**.

[0100] Reactor Systems

[0101] **Fig. 6** is a schematic of a catalytic reaction **600** for the formation of CNTs

5 on a catalyst particle **602**. In some embodiments, the catalytic reaction **600** takes place in a fluidized bed reactor discussed further with respect to **Fig. 7**. An initial reaction **604** between a portion of the compounds containing C, O, and H in the hot gas feed stream **606**, such as the CH₄ and the CO₂, results in the formation of CO and H₂. Excess amounts of the source gases continue to flow through the reactor,

10 helping to fluidize the bed and carrying away CNTs **608** and catalyst particles **610**.

[0102] The reactions that form the CNTs **608** take place on the catalyst particle **602**. Without being bound by theory, a nucleus of iron atoms of sufficient size on the catalyst surface may form the nucleating point for the growth of the carbon products on the catalyst particle **602**. Many parameters affect the morphology of the final

15 product, including reaction temperature, pressure, and feed gas composition.

[0103] The CO and H₂ react on the surface at point **614**, lifting active catalyst particles **616** off the catalyst particle **602**, and forming H₂O **618** and the solid carbon of the CNTs **608**. The CNTs **608** then break off from the catalyst particle **602**.

Larger catalyst particles **602** can be captured and returned to the reactor, for

20 example, by a catalyst separator discussed further with respect to **Fig. 7**, while very fine catalyst particles **602** will be carried out with the CNTs **608**. The final product will include about 70 mol % solid carbon and about 15 mol % metal, about 80 mol % solid carbon and about 10 mol % metal, about 90 mol % solid carbon and about 7 mol % metal, or about 95 mol % solid carbon and about 5 mol % metal. The CNTs

25 **608** will often agglomerate to form clusters **620**, which are the common form of the final product. Some amount of the CO and H₂ passes through the reactor without reacting and are contaminants in the reactor effluent streams.

[0104] As the reaction proceeds, the catalyst particle **602** is degraded and finally consumed. Accordingly, the reaction may be described as a metal dusting reaction.

30 In some embodiments, metal surfaces are protected from attack by a ceramic lining,

since the metal surfaces in contact with the reaction conditions would not only degrade, but may also result in the formation of poorer quality products.

[0105] The catalyst particle **602** can include any number of metals from different IUPAC Groups on the periodic table, such as Group 10 (e.g., nickel), Group 8 (e.g., iron or ruthenium), Group 9 (e.g., cobalt), or Group 6 (e.g., chromium or molybdenum), among others. Other metals that may be present include Group 7 metals (e.g., manganese), or Group 5 metals (e.g., cobalt), among others. It can be understood that the metals listed above are merely exemplary of the Groups mentioned and other metals from those Groups may be included. However, the catalytic sites on the catalyst particles **602** are principally composed of iron atoms. In one embodiment, the catalyst particles **602** include metal shots, for example, groups of about 25-50 mesh metal beads that are used for shot blasting.

[0106] **Fig. 7** is a drawing of a fluidized bed reactor **700** for forming CNTs **702**. A hot gas feed stream **704** is fed through a line **706** into the bottom of the fluidized bed reactor **700**. A control valve **708** may be used to regulate the flow of the hot gas feed stream **704** into the reactor. The hot gas feed stream **704** flows through a distributor plate **710** and will fluidize a bed of catalyst particles **712** held in place by the reactor walls **714**. As used herein, "fluidize" means that the catalyst particles **712** will flow around each other to let gas bubbles through, providing a fluid-like flow behavior. As discussed herein, the reaction conditions are very harsh to any exposed metal surface, as the metal surface will perform as a catalyst for the reaction. Thus, the reaction will result in the slow degradation of an exposed metal surface. Accordingly, the interior surface of the reactor, including the reactor walls **714** and head **715**, as well as the distributor plate **710**, and other parts, can be made of a protective material, such as ceramic or gold, to protect the surfaces.

[0107] As the hot gas feed stream **704** flows through the fluidized bed of catalyst particles **712**, CNTs **702** will form from catalyst particles **712**. The flowing hot gas feed stream **704** carries the CNTs **702** into an overhead line **716** where they are removed from the reactor **700**. Depending on the flow rate, for example, as adjusted by the control valve **708**, some amount of catalyst particles **712** may be carried into

the overhead line **716**. In addition, the flowing hot gas feed stream **704** may include gaseous components, metal residues, and other impurities that are also carried into the overhead line **716** along with the CNTs **702**.

[0108] In various embodiments, a catalyst separator **718** may be configured to
5 separate catalyst particles **712** of a certain size or larger from a reactor effluent stream **720** and return them to the reactor **700** through a recycle line **722**. Any number of configurations may be used for the catalyst separator, including a cyclonic separator, a magnetic separator, a settling tank, or the like.

[0109] Further, a CNT separator **724** may be configured to isolate the CNTs **702**
10 from the reactor effluent stream **720** in order to obtain a final CNT product **726**. A stream **728** containing gaseous components, some residual CNTs, or other impurities is generated from the reactor effluent stream **720** by the isolation of the CNTs **702**. In some embodiments, the CNT separator **724** may include a cyclonic separator, a multicyclonic separator, an electrostatic precipitator, a magnetic
15 separator, an inertial separator, or a gravity separator, among others. The CNT separator may also include a filter, such as a sintered ceramic filter or a sintered metal filter, among others.

[0110] **Fig. 8** is a schematic of a separation system **800** in which a cyclonic separator **802** and a filter **804** are used to isolate the CNTs **702** from the reactor
20 effluent stream **720**. Like numbered items are as described with respect to **Fig. 7**. The cyclonic separator **802** and the filter **804** may be implemented within the CNT separator **724** discussed with respect to **Fig. 7**.

[0111] In various embodiments, the walls of the cyclonic separator **802** may be coated with a protective material with a high temperature resistance, such as
25 ceramic or gold. This may help to protect the cyclonic separator **802** from degradation as a result of the high-temperature of the reactor effluent stream **720**.

[0112] As the reactor effluent stream **720** enters the cyclonic separator **802**, a swirl element within the cyclonic separator **802** may impart a radial acceleration and a tangential velocity component to the reactor effluent stream **720** through the
30 rotation of twisted swirl vanes. The swirl vanes may be arranged parallel or in series

on the swirl element. The swirling of the reactor effluent stream **720** may cause the CNTs **702**, which are heavier and denser than the other particles within the reactor effluent stream **720**, to migrate to the outer rim of the cyclonic separator **802** and begin traveling in a wide circular path, while the other particles may migrate towards the center of the cyclonic separator **802** and begin traveling in a narrow circular path. As the reactor effluent stream **720** nears the end of the cyclonic separator **802**, the CNTs **702** may be captured and sent out of the cyclonic separator **802** as the final CNT product **726**. A stream **806** containing gaseous components, as well as some amount of the CNTs **702** that were not captured by the cyclonic separator **802**, may also be sent out of the cyclonic separator **802**.

[0113] In various embodiments, the stream **806** may be sent to the filter **804**. The filter **804** may be used to remove any remaining CNTs **702** from the stream **806**. The removed CNTs **702** may be sent through a CNT feed line **806** to be combined with the final CNT product **726**. The stream **728**, which may be the final waste stream from the separation process, may be sent out of the separation system **724** for further processing.

[0114] The filter **804** may include any of a number of different types of filters. For example, the filter **804** may be a sintered ceramic filter or a sintered metal filter, which may be capable of withstanding the high temperatures of the stream **806**. The filter **804** may also be a fabric bag filter or a fluidized bed filter, among others. The filter **804** may be configured to perform a self-cleaning procedure to remove any remaining CNTs. In some embodiments, the separation system **724** may include two filters, wherein one filter may be online while the other filter is offline and performing the self-cleaning procedure.

[0115] **Fig. 9** is a schematic of a separation system **900** in which a multicyclonic separator **902** is used to isolate the CNTs **702** from the reactor effluent stream **720**. The multicyclonic separator **902** functions similarly to the cyclonic separator **802**. However, the multicyclonic separator **902** includes multiple cyclones **904** arranged in a parallel configuration.

[0116] In various embodiments, the walls of the cyclones **904** are coated with a protective material with a high temperature resistance, such as ceramic or gold. This may help to protect the cyclones **904** from degradation as a result of the high-temperature of the reactor effluent stream **720**.

5 [0117] As the reactor effluent stream **720** enters the multicyclonic separator **902**, the reactor effluent stream **720** is distributed between the cyclones **904**. In various embodiments, the reactor effluent stream **720** is directed to the center of the cyclones **904**, and may be injected into each of the cyclones **904** near the top. A swirl element within each of the cyclones **904** may impart a radial acceleration and a
10 tangential velocity component to the reactor effluent stream **720** through the rotation of twisted swirl vanes. The swirl vanes may be arranged parallel or in series on the swirl element. The swirling of the reactor effluent stream **720** may cause the CNTs **702**, which are heavier and denser than the other particles within the reactor effluent stream **720**, to migrate to the outer rim of each of the cyclones **904** and begin
15 traveling in a wide circular path, while the other particles may migrate towards the center of each of the cyclones **904** and begin traveling in a narrow circular path. As the reactor effluent stream **720** nears the end of each of the cyclones **904**, the CNTs **702** may be captured and sent out of each of the cyclones **904** into a collection chamber **906**. From the collection chamber **906**, the CNTs **702** may be sent out of
20 the multicyclonic separator **902** as the final CNT product **726**.

[0118] A stream **908** containing gaseous components, including some amount of the CNTs **702** that were not captured by the cyclones **904**, may also be sent out of the multicyclonic separator **902**. In various embodiments, the stream **908** may be sent to the filter **804**, as discussed above with respect to **Fig. 8**. The filter **804** may
25 be used to remove any remaining CNTs **702** from the stream **908**.

[0119] **Fig. 10** is a schematic of a separation system **1000** in which an electrostatic precipitator **1002** is used to isolate the CNTs **702** from the reactor effluent stream **720**. The electrostatic precipitator **1002** may remove the CNTs **702** from the reactor effluent stream **720** using the force of an induced electrostatic
30 charge.

[0120] The electrostatic precipitator **1002** may include a number of discharge electrodes **1004**. The discharge electrodes **1004** may be a number of small-diameter metal wires that hang vertically and are attached together in rigid frames. In addition, the electrostatic precipitator **1002** may include collection electrodes **1006**, which are stacks of large flat metal plates or tubes that are oriented vertically. The collection electrodes **1006** have a charge that is the opposite of the charge of the discharge electrodes **1004**. In some embodiments, the collection electrodes **1006** are spaced about 1 cm to 18 cm apart, depending on the amount of CNTs expected to be present. The reactor effluent stream **720** may flow horizontally through the spaces between the discharge electrodes **1004**, and then pass through the collection electrodes **1006**.

[0121] High-voltage equipment **1008** may be used to apply a negative voltage of several thousand volts between the discharge electrodes **1004** and the collection electrodes **1006**. The applied voltage may result in the ionization of the reactor effluent stream **720** as it flows around the discharge electrodes **1004** and the collection electrodes **1006**. Negative ions may flow to the collection electrodes **1006** and charge the CNTs **702** within the reactor effluent stream **720**. The CNTs **702**, following the negative electric field created by the high-voltage equipment **1008**, may then move to the collection electrodes **1006**.

[0122] The CNTs **702** may build up on the collection electrodes **1006** and form a layer. The layer may be prevented from collapsing by the electrostatic pressure. A number of rappers **1010** may impart a vibration to the discharge electrodes **1004** and the collection electrodes **1006**, resulting in the removal of the CNTs **702** from the collection electrodes **1006**. In some embodiments, water sprayers (not shown) are also used periodically to remove the CNTs **702** from the collection electrodes **1006**.

[0123] A number of hoppers **1012** located at the bottom of the electrostatic precipitator **1002** may be used to collect the CNTs **702** that are isolated from the reactor effluent stream **720**. In addition, a large hopper **1014** may be used to combine and temporarily store the CNTs **702** that are collected within the hoppers

1012. The CNTs **702** may then be sent out of the electrostatic precipitator **1002** as the final CNT product **726**.

[0124] Further, a stream **1016** containing gaseous components, including some amount of the CNTs **702** that were not captured by the collection electrodes **1006**,
5 may also be sent out of the electrostatic precipitator **1002**. In various embodiments, the stream **1016** may be sent to the filter **804**, as discussed above with respect to **Figs. 8 and 9**. The filter **804** may be used to remove any remaining CNTs **702** from the stream **1016**.

[0125] Packaging System

10 **[0126]** **Fig. 11** is a simplified process flow diagram of a packaging system **1100** that can package CNTs separated from an effluent stream from a one reactor system. The packaging system **1100** overlaps the lock hopper **522** of the separation system **518** shown in **Fig. 5**, and is used to isolate the CNTs from the process for packaging.

15 **[0127]** The packaging system **1100** is part of a packaging train **1102**. The packaging train **1102** may have a sampling valve **1104** to remove CNTs from the lock hopper **522**. The sampling valve **1104** may be a rotary valve configured to allow a certain amount of CNTs and gas through during a portion of a rotation cycle. In some embodiments, the sampling valve **1104** may be a ball valve configured to open
20 fully for a selected period of time to allow a selected amount of CNTs and gas through, prior to closing fully. The CNTs and gas are allowed to flow into a drum **1106** for purging and cooling.

[0128] After the sampling valve **1104** has closed, a purge stream **1108** may be opened into the drum **1106** to sweep out remaining gases, such as CO, H₂, H₂O, and
25 CH₄. As noted, the purge stream **1108** may be taken from the CO₂ enriched side of the gas fractionation system, for example, as purge gas stream **530**, discussed with respect to **Fig. 5**. The purge outlet stream **1110** will carry some amount of CNTs, and other fine particles, and may be passed through a filter **1112**, prior to being sent back to the process as a purge return **1114**. The filter **1112** may be a bag filter,
30 cyclonic separator, or any other suitable separation system, such as the filter **804**

discussed with respect to **Fig. 8**. After purging is completed, a packaging valve **1116** will open to allow a stream **1118** including CNTs to flow to a filling station **1120** to be packaged in drums or tanks for sale.

[0129] Method

5 **[0130]** **Fig. 12** is a process flow diagram showing a method **1200** for generating CNTs from a feed gas that includes methane and carbon dioxide. The method **1200** begins at block **1202**, at which a mixed C, H, and O feedstock, such as a CO₂ / CH₄ mixture, is obtained. The feed stock may be obtained from any number of sources. As mentioned, the feedstock may include a natural gas harvested from a sub-surface
10 reservoir, an exhaust gas from a power generation plant, or any number of other gases from natural or plant sources. Further, other feedstocks may be used in embodiments, including other materials, such as syngas, CO, H₂, other hydrocarbons, and the like, as long as the overall feed C:H:O ratio falls within the boundary as shown in Figure 2.

15 **[0131]** At block **1204**, the feedstock is combined with a recycle gas obtained from the waste gases generated in the process. As described herein, the recycle gas may be obtained from the waste gases by gas fractionation, which could involve cryogenic low temperature distillation as well as any number of other techniques. At block **1206**, the combined gas stream is heated with waste heat recovered from the
20 reaction process. After heating, at block **1208**, the combined gas stream is reacted with a metal catalyst in a reactor to form the CNTs. At block **1210**, the CNTs are separated from the waste gas. At block **1212**, the separated CNTs are purged, cooled, and packaged to be sent to market.

[0132] At block **1214**, the waste gas is cooled to remove excess water formed
25 during the reaction. As the process is conducted at high temperatures and pressures, an ambient temperature heat exchanger provides sufficient cooling to condense out the water vapor. Some of the cooling from block **1214** can be used to provide some of the heating in block **1206**. The processes described at blocks **1206-1214** will be repeated for each sequential reactor in the reaction system.

[0133] At block **1216**, the waste gas is fractionated into a CO₂ enriched stream and a CH₄ enriched stream. At block **1218**, whichever stream contains the excess reagent can be sold or used as a fuel, while the other stream can be recycled to block **1204** to be reused in the process.

5 [0134] **Fig. 13** is a process flow diagram showing a method **1300** for removing CNTs from a continuous reactor effluent. The method **1300** may be included within the block **1210** discussed with respect to the method **1200**. The continuous reactor effluent may be a gas flow from the reactor that includes the CNTs as well as waste gas.

10 [0135] The method **1300** begins at block **1302** with the isolation of the CNTs from the continuous reactor effluent. The isolation of the CNTs may be performed within a separation system using any number of separation devices. For example, in some embodiments, a cyclonic or multicyclonic separation device may be used to perform an initial separation of the CNTs from the continuous reactor effluent. In other
15 embodiments, a magnetic separation device or an electrostatic precipitator, among others, may be used to perform the initial separation.

[0136] A filtration system may also be used to further separate the CNTs from the continuous reactor effluent. The filtration system may include any number of filters of various types. For example, a sintered ceramic filter, sintered metal filter, fabric
20 bag filter, or fluidized bed filter may be used to filter out any remaining CNTs within the continuous reactor effluent. In various embodiments, at block **1212**, the isolated CNTs may then be sent to the market.

[0137] At block **1304**, a stream containing gaseous components may be generated from the continuous reactor effluent. The stream may be generated
25 through the separation of the CNTs from the continuous reactor effluent. Such a stream containing gaseous components may be the waste gas discussed with respect to **Fig. 12**. Thus, the stream may then be cooled to remove excess water formed during the reaction, fractionated into a CO₂ enriched stream and a CH₄ enriched stream, and either sold or recycled, as discussed with respect to blocks

1214-1218 of **Fig. 12**. In some embodiments, if the stream is recycled, it may be sent back into the fluidized bed reactor to be reused for the creation of the CNTs.

[0138] **Fig. 13** is not intended to indicate that the steps of the method **1300** are to be executed in any particular order, or that all of the steps of the method **1300** are to

5 be included in every case. Further, any number of additional steps may be included within the method **1300**, depending on the specific application. For example, in

some embodiments, a separation system may be used to generate a first purified stream of the CNTs and a first residual stream including gaseous components from the continuous reactor effluent. Then, a filtration system may be used to generate a

10 second purified stream of the CNTs and a second residual stream including impurities from the first purified stream of the CNTs. In addition, the first purified stream and the second purified stream may be combined into a final purified stream of the CNTs.

In some embodiments, a second separation vessel may also be configured to generate an additional purified stream of the CNTs and an additional residual stream

15 from the continuous reactor effluent or the first purified stream of the CNTs, or both.
[0139] Embodiments

[0140] Embodiments of the invention may include any combinations of the methods and systems shown in the following numbered paragraphs. This is not to be considered a complete listing of all possible embodiments, as any number of

20 variations can be envisioned from the description above.
1. A system for removing carbon nanotubes from a continuous reactor effluent, including a separation vessel configured to:

isolate the carbon nanotubes from the continuous reactor effluent; and
generate a stream including gaseous components from the continuous reactor
25 effluent.

2. The system of paragraph 1, wherein the separation vessel is configured to:

isolate catalyst particles from the continuous reactor effluent; and
return the catalyst particles to a reactor.

3. The system of any of paragraphs 1 or 2, wherein the reactor includes a fluidized bed reactor that is configured to accept the catalyst particles from the separation vessel.

4. The system of any of paragraphs 1-3, wherein the stream includes
5 residual carbon nanotubes.

5. The system of any of paragraphs 1-4, wherein the separation vessel includes a gravity separation vessel.

6. The system of paragraph 5, wherein the gravity separation vessel includes a cyclonic separator.

10 7. The system of paragraph 6, wherein the cyclonic separator includes a single cyclone.

8. The system of paragraph 6, wherein the cyclonic separator includes multiple cyclones.

9. The system of paragraph 5, wherein the gravity separation vessel
15 includes a drift separator.

10. The system of any of paragraphs 1-5, wherein the separation vessel includes an electrostatic separation unit configured to impose an electric field.

11. The system of any of paragraphs 1-5 or 10, wherein the separation vessel includes a magnetic separation vessel.

20 12. The system of any of paragraphs 1-5, 10, or 11, wherein the separation vessel includes a filter.

13. The system of paragraph 12, wherein the filter includes a sintered ceramic filter, a sintered metal filter, a fabric bag filter, or a fluidized bed filter, or any combinations thereof.

25 14. The system of paragraph 12, wherein the filter is configured to perform a self-cleaning procedure to remove any remaining carbon nanotubes.

15. A method for removing carbon nanotubes from a continuous reactor effluent, including:

flowing the continuous reactor effluent through a separation vessel;

separating carbon nanotubes from the continuous reactor effluent in the separation vessel; and
generating a stream including gaseous components from the continuous reactor effluent.

5 16. The method of paragraph 15, including isolating the carbon nanotubes from the stream including gaseous components through an electromagnetic separation process.

10 17. The method of any of paragraphs 15 or 16, including isolating the carbon nanotubes from the stream including gaseous components through a gravity separation process.

18. The method of paragraph 17, wherein the gravity separation process includes using a cyclonic separator.

19. The method of paragraph 18, wherein the cyclonic separator includes a multicyclonic separator.

15 20. The method of any of paragraphs 15-17, wherein the separation vessel is configured to generate the carbon nanotubes and the stream including gaseous components through a density based separation process.

20 21. The method of any of paragraphs 15-17 or 20, including:
isolating an excess catalyst stream from the continuous reactor effluent; and
flowing the excess catalyst stream to a reactor.

22. A system for creating a purified stream of carbon nanotubes from a gas flow, including:

25 a separation system configured to generate a first purified stream of the carbon nanotubes and a first residual stream including gaseous components from the gas flow; and

a filtration system configured to generate a second purified steam of the carbon nanotubes and a second residual stream including impurities from the first purified stream of the carbon nanotubes.

30 23. The system of paragraph 22, wherein the separation system is configured to:

isolate an excess reagent stream from the gas flow; and
flow the excess reagent stream to a reactor.

24. The system of any of paragraphs 22 or 23, wherein the separation
system includes a multicyclonic separation system or a single cyclonic separation
5 system.

25. The system of any of paragraphs 22-24, wherein the separation system
includes an electrostatic precipitator.

26. The system of any of paragraphs 22-25, wherein the separation system
includes a magnetic separation system.

10 27. The system of any of paragraphs 22-26, wherein the separation system
includes an inertial separation system.

28. The system of any of paragraphs 22-27, wherein the filtration system
includes a sintered ceramic filtration system, a sintered metal filtration system, a
fabric bag filtration system, or a fluidized bed filtration system, or any combinations
15 thereof.

29. The system of any of paragraphs 22-28, wherein the separation system
includes a wet removal system, and wherein the wet removal system includes a
venturi scrubber, a counter current water scrubber, a steam condensation system, or
a barometric condensation system, or any combinations thereof.

20 30. The system of any of paragraphs 22-29, wherein the system is
configured to combine the first purified stream and the second purified stream into a
final purified stream of the carbon nanotubes.

31. The system of any of paragraphs 22-30, including a second separation
vessel configured to generate an additional purified stream of the carbon nanotubes
25 and an additional residual stream including gaseous components from the gas flow
or the first purified stream of the carbon nanotubes, or both.

[0141] While the present techniques may be susceptible to various modifications
and alternative forms, the embodiments discussed above have been shown only by
way of example. However, it should again be understood that the techniques is not
30 intended to be limited to the particular embodiments disclosed herein. Indeed, the

present techniques include all alternatives, modifications, and equivalents falling within the true spirit and scope of the appended claims.

CLAIMS

What is claimed is:

1. A system for removing carbon nanotubes from a continuous reactor effluent, comprising a separation vessel configured to:
5 isolate the carbon nanotubes from the continuous reactor effluent; and
generate a stream comprising gaseous components from the continuous reactor effluent.
- 10 2. The system of claim 1, wherein the separation vessel is configured to:
isolate catalyst particles from the continuous reactor effluent; and
return the catalyst particles to a reactor.
- 15 3. The system of claim 2, wherein the reactor comprises a fluidized bed reactor that is configured to accept the catalyst particles from the separation vessel.
4. The system of claim 1, wherein the stream comprises residual carbon nanotubes.
- 20 5. The system of claim 1, wherein the separation vessel comprises a gravity separation vessel.
- 25 6. The system of claim 5, wherein the gravity separation vessel comprises a cyclonic separator.
7. The system of claim 6, wherein the cyclonic separator comprises a single cyclone.
8. The system of claim 6, wherein the cyclonic separator comprises
30 multiple cyclones.

9. The system of claim 5, wherein the gravity separation vessel comprises a drift separator.

5 10. The system of claim 1, wherein the separation vessel comprises an electrostatic separation unit configured to impose an electric field.

11. The system of claim 1, wherein the separation vessel comprises a magnetic separation vessel.

10

12. The system of claim 1, wherein the separation vessel comprises a filter.

13. The system of claim 12, wherein the filter comprises a sintered ceramic filter, a sintered metal filter, a fabric bag filter, or a fluidized bed filter, or any combinations thereof.

15

14. The system of claim 12, wherein the filter is configured to perform a self-cleaning procedure to remove any remaining carbon nanotubes.

20

15. A method for removing carbon nanotubes from a continuous reactor effluent, comprising:

flowing the continuous reactor effluent through a separation vessel;

separating carbon nanotubes from the continuous reactor effluent in the

25

separation vessel; and

generating a stream comprising gaseous components from the continuous reactor effluent.

16. The method of claim 15, comprising isolating the carbon nanotubes from the stream comprising gaseous components through an electromagnetic separation process.

5 17. The method of claim 15, comprising isolating the carbon nanotubes from the stream comprising gaseous components through a gravity separation process.

10 18. The method of claim 17, wherein the gravity separation process comprises using a cyclonic separator.

19. The method of claim 18, wherein the cyclonic separator comprises a multicyclonic separator.

15 20. The method of claim 15, wherein the separation vessel is configured to generate the carbon nanotubes and the stream comprising gaseous components through a density based separation process.

20 21. The method of claim 15, comprising:
isolating an excess catalyst stream from the continuous reactor effluent; and
flowing the excess catalyst stream to a reactor.

22. A system for creating a purified stream of carbon nanotubes from a gas flow, comprising:

25 a separation system configured to generate a first purified stream of the carbon nanotubes and a first residual stream comprising gaseous components from the gas flow; and
a filtration system configured to generate a second purified stream of the carbon nanotubes and a second residual stream comprising impurities
30 from the first purified stream of the carbon nanotubes.

23. The system of claim 22, wherein the separation system is configured to:

5 isolate an excess reagent stream from the gas flow; and
flow the excess reagent stream to a reactor.

24. The system of claim 22, wherein the separation system comprises a multicyclonic separation system or a single cyclonic separation system.

10 25. The system of claim 22, wherein the separation system comprises an electrostatic precipitator.

26. The system of claim 22, wherein the separation system comprises a magnetic separation system.

15 27. The system of claim 22, wherein the separation system comprises an inertial separation system.

28. The system of claim 22, wherein the filtration system comprises a
20 sintered ceramic filtration system, a sintered metal filtration system, a fabric bag filtration system, or a fluidized bed filtration system, or any combinations thereof.

29. The system of claim 22, wherein the separation system comprises a wet removal system, and wherein the wet removal system comprises a venturi
25 scrubber, a counter current water scrubber, a steam condensation system, or a barometric condensation system, or any combinations thereof.

30. The system of claim 22, wherein the system is configured to combine the first purified stream and the second purified stream into a final purified stream of
30 the carbon nanotubes.

31. The system of claim 22, comprising a second separation vessel configured to generate an additional purified stream of the carbon nanotubes and an additional residual stream comprising gaseous components from the gas flow or the
5 first purified stream of the carbon nanotubes, or both.