

METHOD AND SYSTEMS FOR FORMING CARBON NANOTUBES

RELATED APPLICATIONS

[0001] This application claims priority to United States Provisional Patent Application Serial No. 61/569,494 by Denton and Noyes and titled "Methods and System for Forming Carbon Nanotubes," which was filed 12 December 2011, and to United States Provisional Patent Application Serial No. 61/582,098 by Denton and Noyes and titled "Method and Systems for Forming Carbon Nanotubes," which was filed 30 December 2011.

FIELD

[0002] The present techniques relate to an industrial scale process for forming carbon fibers and carbon nanomaterials.

BACKGROUND

[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 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 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 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.

[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 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 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. 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/min. Another technique described uses laser 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 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 the high productivity that 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. The process is conducted at a low pressure and uses a cryogenic chilling process to remove water from a feed stream.

[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 and the process efficiencies are both low.

SUMMARY

[0011] An embodiment described herein provides a system for the production of carbon nanotubes. The system includes a feed gas heater configured to heat a feed gas with waste heat from a waste gas stream, a reactor configured to form carbon nanotubes from the feed gas in a Bosch reaction, a separator configured to separate the carbon nanotubes from the reactor effluent stream forming the waste gas stream, and a water removal system. The water removal system includes an ambient temperature heat exchanger and separator configured to separate the bulk of the water from the waste gas stream to form a dry waste gas stream.

[0012] Another embodiment provides a method for forming carbon nanotubes. The method includes forming carbon nanotubes in a reactor using a Bosch reaction, separating the carbon nanotubes from a reactor effluent to form a waste gas stream, and heating the feed gas, a dry waste gas stream, or both, with waste heat from the waste gas stream. The waste gas stream is chilled in an ambient temperature heat exchanger to condense water vapor, forming the dry waste gas stream.

[0013] Another embodiment provides a reaction system for forming carbon nanotubes. The reaction system includes two or more reactors configured to form carbon nanotubes from gas streams using a Bosch reaction, wherein an effluent from each reactor, before a final reactor, is used as a feed stream for a downstream reactor. An effluent stream from the final reactor includes a reactant depleted waste stream. A separation system is disposed downstream of each reactor, wherein the separation system is configured to remove carbon nanotubes from the effluent from the reactor. A

feed heater is disposed downstream of each separation system, wherein the feed heater includes a heat exchanger configured to heat a feed gas stream for a following reactor using waste heat from the effluent from the reactor, and wherein the feed heater downstream of the final reactor is configured to heat a gas stream for the first reactor. An ambient temperature heat exchanger is located downstream of each feed heater, wherein the ambient temperature heat exchanger is configured to remove water from the effluent, forming the feed stream for the following reactor. A compressor is configured to increase the pressure of the reactant depleted waste stream. An ambient temperature heat exchanger located downstream of the compressor is configured to remove water from the reactant depleted waste stream. A gas fractionation system is configured to separate the reactant depleted waste stream into a methane enriched stream and a carbon dioxide enriched stream, and a mixer is configured to blend the methane enriched stream or the carbon dioxide enriched stream into an initial feed stream.

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 nanotubes, for example, as a by-product of a carbon dioxide sequestration reaction;

[0016] **Fig. 1A** is a block diagram of the use of an excess carbon dioxide feed in an enhanced oil recovery (EOR) process;

[0017] **Fig. 1B** is a block diagram of the use of an excess methane feed in a power generation process;

[0018] **Fig. 2** is a C-H-O equilibrium diagram of the equilibria between carbon, hydrogen, and oxygen, indicating species in equilibrium at various temperature conditions;

[0019] **Fig. 3** is a simplified process flow diagram of a one reactor system for making carbon nanotubes from a gas feed that includes carbon dioxide and methane;

[0020] **Fig. 4** is a simplified process flow diagram of a two reactor system for making carbon nanotubes from a gas feed that includes carbon dioxide and methane;

[0021] **Fig. 5** is a simplified process flow diagram of a one reactor system for making carbon nanotubes from a gas feed that includes carbon dioxide and methane, in which the carbon dioxide is in excess;

[0022] **Figs. 6A, 6B, and 6C** are simplified process flow diagrams of a two reactor system for making carbon nanotubes from a gas feed that includes carbon dioxide and methane, in which the carbon dioxide is in excess;

[0023] **Fig. 7** is a simplified process flow diagram of a one reactor system for making carbon nanotubes from a gas feed that includes carbon dioxide and methane, in which the methane is in excess;

[0024] **Figs. 8A, 8B, and 8C** are simplified process flow diagrams of a two reactor system for making carbon nanotubes from a gas feed that includes carbon dioxide and methane, in which the methane is in excess;

[0025] **Fig. 9** is a drawing of a fluidized bed reactor for forming carbon nanotubes;

[0026] **Fig. 10** is a schematic of a catalytic reaction for the formation of carbon nanotubes on a catalyst bead;

[0027] **Fig. 11** is a simplified process flow diagram of a gas fractionation process that can be used to separate excess carbon dioxide feed in a reactor system for the production of carbon nanotubes;

[0028] **Fig. 12** is a simplified process flow diagram of a packaging system that can package carbon nanotubes separated from a reactor effluent stream from a one reactor system;

[0029] **Fig. 13** is a simplified process flow diagram of a packaging system that can package carbon nanotubes separated from each reactor effluent stream in a two reactor system; and

[0030] **Fig. 14** is a method for generating carbon nanotubes from a feed gas that includes methane and carbon dioxide.

DETAILED DESCRIPTION

[0031] 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 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.

[0032] 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 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 scope of the present claims.

[0033] 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 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. It can be understood that the term "carbon nanotubes" as used herein and in the claims, includes other allotropes of carbon, such as carbon fibers, carbon nanofibers, and other carbon nanostructures.

[0034] 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 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.

[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, 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] A “hydrocarbon” is an organic compound that primarily includes the elements hydrogen and carbon, although nitrogen, sulfur, oxygen, metals, or any 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.

[0037] 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 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., hydrogen sulfide), or any combination 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.

[0038] A “low-BTU natural gas” is a gas that includes a substantial proportion of CO₂ as harvested from a reservoir. For example, a low BTU natural gas may include 10 mol % or higher CO₂ in addition to hydrocarbons and other components. In some cases, the low BTU natural gas may include mostly CO₂.

[0039] Overview

[0040] Embodiments described herein provide systems and methods for making carbon fibers, nanofibers, and nanotubes (CNTs) on an industrial scale 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, the feedstocks are higher in CO₂. Other feedstocks may be used, including mixtures of H₂, CO, CO₂, and other hydrocarbons. The process is conducted under high temperature and pressure conditions using a Bosch reaction, as discussed with respect to **Fig. 2**.

[0041] The process may be slightly exothermic, energy neutral, or slightly endothermic. Accordingly, at least a portion of the heat from the reaction 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 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 this reagent to the process.

[0042] 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 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 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.

[0043] Embodiments described herein can be used to produce industrial quantities of carbon products such as fullerenes, carbon nanotubes, carbon nanofibers, carbon fibers, graphite, carbon black, and graphene, among others, using carbon oxides as the primary carbon source. The balance of the possible products may be adjusted by the conditions used for the reaction, including catalyst compositions, temperatures, pressures, feedstocks, and the like. In a reactor system, the carbon oxides are catalytically converted to solid carbon and water. The carbon oxides may be obtained from numerous sources, including the atmosphere, combustion gases, process off-gases, well gas, and other natural and industrial sources.

[0044] The present process uses two feedstocks, a carbon oxide, e.g., carbon dioxide (CO_2) or carbon monoxide (CO), and a reducing agent, e.g., methane (CH_4) or other hydrocarbons, hydrogen (H_2), or combinations thereof. The reducing agent may include other hydrocarbon gases, hydrogen (H_2), 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, may be 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 (H_2) and, thus, includes both the carbon oxide and the reducing gas in a single mixture. Syngas may be used as all or a portion of the feed gas.

[0045] 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 often have

much higher concentrations and are 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.

[0046] The systems described herein may be incorporated into power production and industrial processes for the sequestration of carbon oxides, allowing their conversion to solid carbon products. For example, the carbon oxides in the combustion or process off-gases may be separated and concentrated to become a feedstock for this process. In some cases these methods may be incorporated directly into the process flow without separation and concentration, for example as an intermediate step in a multi-stage gas turbine power station.

[0047] **Fig. 1** is a block diagram of a reaction system **100** that generates carbon structures, for example, as a by-product of a carbon dioxide sequestration reaction. The reaction system **100** is provided a feed gas **102**, which can be a mixture of CO₂ and CH₄. In some embodiments, the reaction may allow for sequestration of 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.

[0048] The feed gas **102** is passed through a heat exchanger **104** to be heated for reaction. During continuous operation, a portion of the heating is provided using heat **106** 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 appropriate reaction temperature, e.g., about 930-1832 °F (about 500-1000 °C). In one embodiment, the feed is heated to about 1650 °F (around 900 °C). The heated feed gas **108** is fed to a reactor **110**.

[0049] In the reactor **110**, a catalyst reacts with a portion of the heated feed gas **108** to form carbon nanotubes **112** using the Bosch reaction. 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 carbon nanotubes **112** are separated from the flow stream **114** out of the reactor **110**, leaving a waste gas stream **116** containing excess reagents and water vapor. At least a portion of the heat from the flow stream **114** is used to form the heated feed gas **108** prior to the flow stream **114** entering the chiller as the waste gas stream **116**.

[0050] The waste gas stream **116** is passed through an ambient temperature heat exchanger, such as water chiller **118**, which condenses out the water **120**. The resulting dry waste gas stream **122** is used as a feed stream for a gas fractionation system **124**. 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 waste gas stream may be greater than about 10 °C, greater than about 20 °C, or higher. A dryer may be used to lower the dewpoint, for example, to -50 °C or lower, prior to gas fractionation.

[0051] The gas fractionation system **124** 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 **126** with the feed gas **102**. The higher concentration gas in the feed gas **102** can be disposed of as excess feed **128**, 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 **124** can be used to remove CH₄ remaining in the waste gas stream, and send it back into the process as recycle **126**. 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 **124** 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 **128** 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, as discussed with respect to **Fig. 1C**.

[0052] **Fig. 1A** is a block diagram of the use of an excess carbon dioxide feed in an enhanced oil recovery (EOR) process. If the excess feed gas **102 (Fig. 1)** is CO₂, the excess feed **128** may be sold to a distributor for marketing through a pipeline **130**. Individual users may obtain the CO₂ from the pipeline **130** and use it in enhanced oil recovery processes **132**. For example, the CO₂ can be used to pressurize hydrocarbon reservoirs to increase the recovery of hydrocarbons.

[0053] **Fig. 1B** is a block diagram of the use of an excess methane feed in a power generation process. If the excess feed gas **102 (Fig. 1)** is CH₄, the excess feed **128** can be used in a power plant **134** to generate power, either on-site, or after transporting the excess feed **128** through a pipeline to the power plant **134**. The electricity **136** generated in the power plant **134** can be used on-site to power the reaction system **100** or may be provided to a grid for use by other consumers. The excess feed **128** can contain a number of other gases as by-products of the CNT formation process, and, thus, the excess feed **128** may be purified prior to any commercial sales, such as to a pipeline company.

[0054] **Fig. 2** is a C-H-O equilibrium diagram **200** of the equilibria between carbon **202**, hydrogen **204**, and oxygen **206**, indicating species in equilibrium at various temperature conditions. There is a spectrum of reactions involving these three elements in which various equilibria have been named as reactions. The equilibrium lines at various temperatures that traverse the diagram show the approximate regions in which solid carbon will form. For each temperature, solid carbon will form in the regions above the associated equilibrium line, but will not form in the regions below the equilibrium line.

[0055] Hydrocarbon pyrolysis is an equilibrium reaction between hydrogen and carbon that favors solid carbon production, typically with little or no oxygen or water present, e.g., along the equilibrium line **208** from higher hydrogen **204** content to higher

carbon **202** content. The Boudouard reaction, also called the carbon monoxide disproportionation reaction, is an equilibrium reaction between carbon and oxygen that favors solid carbon production, typically with little or no hydrogen or water present, and is along the equilibrium line **210**, from higher oxygen **206** content to higher carbon **202** content.

[0056] The Bosch reaction is an equilibrium reaction that favors solid carbon production when carbon, oxygen, and hydrogen are present. In the C-H-O equilibrium diagram **200**, the Bosch reactions are located in the interior region of the triangle, for example, in region **212**, where equilibrium is established between solid carbon and reagents containing carbon, hydrogen, and oxygen in various combinations. Numerous points in the Bosch reaction region **212** favor the formation of CNTs and several other forms of solid carbon product. The reaction rates and products may be enhanced by the use of a catalyst, such as iron. The selection of the catalysts, reaction gases, and reaction conditions may provide for the control of the type of carbon formed. Thus, these methods open new routes to the production of solid carbon products such as CNTs.

[0057] Reaction Systems

[0058] **Fig. 3** is a simplified process flow diagram of a one reactor system **300** for making carbon nanotubes 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** for a higher CO₂ content feed gas and **Figs. 7** and **8** for a higher CH₄ content feed gas. In the reaction 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**.

[0059] 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 about 90 °F (about 32.2 °C) to about 1400 °F (about

760 °C) 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. 9**. In the fluidized bed reactor **318**, carbon nanotubes are formed on catalyst particles. The catalyst particles and reactions are further discussed with respect to **Fig. 10**.

[0060] The carbon nanotubes are carried from the first fluidized bed reactor **318** in a reactor effluent stream **320**. The reactor effluent stream **320** may be at a temperature of about 1650 °F (about 900 °C) 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 device **322**, such as a cyclonic separator, to remove the carbon nanotubes **324**. The resulting 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 in secondary separation devices (not shown) at lower temperatures than the waste gas stream **326**.

[0061] 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** is at around 100 °F (about 38 °C) and at a pressure of about 540 psia (about 3,720 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** to about 1050 psia (about 7,240 kPa) forming a high pressure stream **340** which is passed through another ambient 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.

[0062] 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.

[0063] The reaction conditions used can cause significant degradation of metal surfaces, as indicated by choice of the catalyst itself, which may include stainless steel beads. 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.

[0064] **Fig. 4** is a simplified process flow diagram of a two reactor system **400** for making carbon nanotubes 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 (not shown) 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**.

[0065] 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 100 °F (about 38 °C).

[0066] The reactant stream **412** passes through the heat exchanger **404** and is heated by waste heat from the waste gas stream **402**. The heated stream **414** is then fed to a second fluidized bed reactor **416** in which additional carbon nanotubes are formed. However, the heated stream **414** may not be at a sufficiently high temperature, e.g., greater than about 1600 °F (about 871 °C), to form carbon nanotubes in the second fluidized bed reactor **416**. To increase the temperature of the heated stream **414**, a second 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 separator **422**, such as a cyclonic separator, to separate carbon products from the second reactor effluent stream **420**. 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**.

[0067] Although only two fluidized bed reactors **318** and **416** are shown in this 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 the sequence. Further, the reactors do not have to be fluidized bed reactors, as other configurations may be used in 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 divide the dried gas stream **346** into the excess feed **350** and a recycle gas **304**.

[0068] **Fig. 5** is a simplified process flow diagram of a one reactor system **500** for making carbon nanotubes 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**. The numbered diamonds in the process correspond to simulated process values, as provided in Table 1 for a higher CO₂ content feed gas **302**. 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**.

[0069] In this embodiment, the heated gas stream **312** is raised to a temperature of about 800 °F (about 427 °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 arrows **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 about 1540 °F (838 °C).

[0070] 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**.

[0071] 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 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 are formed in the fluidized bed reactor **318**, and carried out in the reactor effluent stream **320**.

[0072] TABLE 1: Process values for Higher Carbon Dioxide Feed for One Reactor System

No.	Contents (% are mol %)	T °F (°C)	P PSIA (kPa)	Flow MSCFD (m ³ /hr)
1	20 % CH ₄ / 80 % CO ₂	100 (37.8)	590 (4,068)	42 (49,553)
2	Recycle Gas 98 % CH ₄ / 2 % CO ₂	50 (23.9)	590 (4,068)	154 (182,000)
3		74 (23.3)		
4		667 (352.8)		
5		1529 (832)		
6	20 % CH ₄ / 49 % CO ₂ 23 % CO / 8.2 % H ₂	1650 (899)	570 (3,930)	84 (99,106)
7		1579 (859)		
8		791 (422)		
9	Carbon nanotubes			162.7 tons/day (182,000 kg/day)
10	Purge return	150-700 (66 – 371)	550 (3,792)	< 0.1 (<118)
11	Water			53 GPM (201 L/min)
12		100 (37.8)	550 (3,792)	
13	Compression energy in			8990 BHP (3,190 kW)
14			1,320 (9,100)	
15	H ₂ O			0.2 GPM (0.8 L/min)
16		100 (37.8)	1,310 (9032)	72 (85,000)
17	1 % CH ₄ / 99 % CO ₂	63 (17)	2000 (13,800)	23 (27,100)
18	Purge gas	41-45 (5-7)	602 (4,151)	< 0.1 (<118)
19	Fuel Gas	50 (10)	590 (4,068)	5.4 (6,371)

[0073] After flowing through the second ceramic block heater **510**, the reactor effluent **320** is flowed to a separation system **518**, which is used to remove the CNTs from the reactor effluent **320**. In this embodiment, the separation system **518** for the CNTs includes a cyclonic separator **520**, a lock hopper **522**, and a filter **524**. 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 from the waste gas stream **526**. This may help to prevent plugging, or other problems, caused by residual CNTs in the waste gas stream **526**. The filter **524** can include bag filters, sintered metal filters, and ceramic filters, among other types. From the CNT separation systems **518**, the CNTs may be directed to a packaging system, as discussed in further detail with respect to **Fig. 10**. 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 water. After flowing through the separation vessel **332**, the flow is as described with respect to **Fig. 3**.

[0074] 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** and sent to a power plant, such as power plant **134** (**Fig. 1**). 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**.

[0075] **Figs. 6A, 6B, and 6C** are simplified process flow diagrams of a two reactor system **600** for making carbon nanotubes from a gas feed that includes carbon dioxide and methane, in which the carbon dioxide is in excess. Like numbered items are as described with respect to **Figs. 3** and **5**. The primary difference between the embodiment illustrated in **Fig. 5** and that shown in **Figs. 6A-6C** is the use of a second reactor to provide another amount of CNTs from remaining reactants in the effluent from the first reactor.

[0076] As described with respect to the one reactor system **500** (**Fig. 5**), the flow begins when the feed gas **302** is blended with a recycle gas **304** in a static mixer **304**. The combined gas stream **308** is passed through a heat exchanger **602** to be heated by a hot waste gas stream from a reactor effluent. The heat exchanger **602** may be similar to that described for heat exchanger **310** in **Fig. 5**. From the heat exchanger **602**, the heated gas stream **312** passes through a second heat exchanger **604**, which can use ceramic block heat exchangers **506** and **510** to further heat the heated gas stream **312**, as described for the second heat exchanger **504** of **Fig. 5**. The resulting high temperature heated gas stream **312** can be further heated in a package heater to form the hot gas stream **316**, which can be fed to the fluidized bed reactor **318**. CNTs are formed in the fluidized bed reactor **318**, and carried out in the reactor effluent stream **320**.

[0077] The reactor effluent stream **320** can be flowed into a heat exchanger **606**, in which the flow is cooled in a ceramic block heat exchanger **510**, as indicated by arrows **512**. From the heat exchanger **606**, the cooled effluent stream **607** can be flowed to a separation system **608** in which the CNTs are separated from the cooled effluent stream **607**, for example, in a cyclonic separator **520**, as described with respect to **Fig. 5**. The resulting waste gas stream **609** can be flowed through a filter **524** in the separation system **608** to remove most of the remaining CNTs. After the filter **524**, the waste gas stream **609** is flowed through the heat exchanger **610** before flowing to the ambient temperature heat exchanger **612** and flowing to a separation vessel **614** for separation of the water. The resulting dry stream **616** can then be flowed through the heat exchanger **610** to be heated by exchanging heat with the waste gas stream **609**. The heat exchanger **610** may include shell-and-tube heat exchangers **422** that, in this case, raise the temperature of the dry stream **616** from about 100 °F (about 37.8 °C), at point 11, to about 715 °F (about 379.4 °C) at point 12. The heated gas stream **618** is further heated by flowing through a ceramic block heater **506** in a second heat exchanger **606**.

[0078] A package heater **622** may be used to provide a further amount of heat to bring the heated gas stream **618** up to a temperature sufficient for reaction. The final hot gas stream **624** is fed to a second fluidized bed reactor **626**, which forms another aliquot of CNTs.

[0079] The CNTs are carried out of the second fluidized bed reactor **626** in a reactor effluent stream **628**, which is flowed through a second ceramic block heat exchanger **510** for cooling. From the second ceramic block heat exchanger **510**, the effluent stream **630** is flowed to a separation system **632**, as described for separation system **608**. After a filter **524** in the separation system **632** removes CNTs from the waste gas stream **634**, the waste gas stream **634** is passed through the heat exchanger **602** for further cooling. The resulting waste gas stream **526** is passed to the ambient temperature heat exchanger **330** to condense out the water.

[0080] The ceramic block heat exchangers **506** in the second heat exchanger **606** are configured to have an exchanged flow, as discussed with respect to the second heat exchanger **504** in **Fig. 5**. Other portions of the system **600** are similar to that described with respect to **Figs. 3** and **5**, although the process values can differ. Relevant process values for the system are shown in Table 2 or Table 3 for simulations of the two reactor system. Furthermore, more than two reactor systems may also be used in embodiments.

[0081] As discussed with respect to the previous figures, after the removal of a final aliquot of water from the high pressure stream **340** in a third separation vessel **344**, the dried gas stream **346** is sent to a gas fractionation system **348**, which can remove a high methane recycle gas **304** from a CO₂ waste stream **350**. The gas fractionation system **348** is discussed further with respect to **Fig. 11**.

[0082] TABLE 2: Process values for Higher Carbon Dioxide Feed for Two Reactor System

No.	Contents (% are mol %)	T °F (°C)	P PSIA (kPa)	Flow MSCFD (m ³ /hr)
1	20 % CH ₄ / 80 % CO ₂	100 (37.8)	590 (4,068)	52 (61,351)
2	98 % CH ₄ / 2 % CO ₂	75 (23.9)	590 (4,068)	154 (182,000)
3		766 (408)		
4		1539 (837)		
5	51 % CH ₄ / 49 % CO ₂	1620 (882)	570 (3,930)	207 (244,000)
6		1624 (884)		
7		800 (427)		
8	Carbon nanotubes			162.7 tons/day (148,000 kg/day)
9	Purge return	150-700 (66 – 371)	550 (3,792)	< 0.1 (<118)
10	Water			39 GPM (148 L/min)
11		100 (37.8)		
12		715 (349.4)		
13		1599 (870.6)	540 (3,723)	
14		1603 (872.8)		
15		800 (427)		
16	Carbon nanotubes			57.5 tons/day (52,000 kg/day)
17	Water			14 GPM (53 L/min)
18		100 (37.8)	520 (3,585)	
19	Compression energy in			8990 BHP (6,700 kW)
20			1,075 (7,412)	
21	H ₂ O			0.6 GPM (2.3 L/min)
22		100 (37.8)	1,065 (7,343)	193 (228,000)
23	1 % CH ₄ / 99 % CO ₂	40 (4.4)	502 (3461)	34 (40,114)
24	Purge gas	75 (23.9)	592 (4082)	< 0.1 (<118)
25	Fuel Gas	75 (23.9)	590 (4068)	4.3 (5,100)

[0083] TABLE 3: Process values for Higher Carbon Dioxide Feed for Two Reactor System

No.	Contents (% are mol %)	T °F (°C)	P PSIA (kPa)	Flow MSCFD (m ³ /hr)
1	20 % CH ₄ / 80 % CO ₂	100 (37.8)	590 (4,068)	42 (49,600)
2	9.88 % CH ₄ / 19.23 % CO ₂ 58.5 % CO/ 12.4 % H ₂	65 (18.3)	590 (4,068)	18.2 (21,500)
5	17 % CH ₄ / 62 % CO ₂ 58.5 % CO/ 12.4 % H ₂	1,650 (899)	570 (3,930)	60.3 (71,100)
6		1,515 (824)	570 (3,930)	62.4 (73,600)
8	Carbon nanotubes			134 tons/d (122,000 kg/day)
13	9 % CH ₄ / 57 % CO ₂ 24 % CO/ 6.9 % H ₂	1,600 (871)	530 (3,654)	
14	4.9 % CH ₄ / 50.5 % CO ₂ 27.0 % CO/ 5.7 % H ₂	1,552 (844)	570 (3,930)	
16	Carbon nanotubes			63.0 tons/d (57,000 kg/day)
20			1,075 (7,412)	
17	H ₂ O			0.6 GPM (2.3 L/min)
18		100 (37.8)	1,065 (7,343)	193 (228,000)
23	1 % CH ₄ / 99 % CO ₂	63 (17.2)	2,000 (13,790)	25 (29,500)
25	FUEL GAS	65 (18.3)	590 (4,068)	7.2 (8,495)

[0084] The individual streams 304 and 350 can be used to supply other gases for the process. For example, a fuel gas stream 528 may be removed from the high methane recycle gas 304 and used for powering turbines, boilers, or other equipment in order to provide power to the system 600 or to an electric grid. Further, a purge gas stream 530 may be removed from the CO₂ waste stream 350. The purge gas stream 530 may be used for cooling and purging the CNTs, as described with respect to Fig. 12. The purge gas may also be used for various cleaning functions in the plant, such as blowing residual CNTs out of a ceramic heat exchanger 506 or 510 when flow is reversed.

[0085] The process conditions shown in Tables 2 and 3 are merely intended to be examples of conditions that may be found in a plant, as determined by simulations. The actual conditions may be significantly different and may vary significantly from the conditions shown. A similar plant configuration may be used for a high methane feed gas, as discussed with respect to **Figs. 7 and 8**. Further, the recycle and effluent waste streams can contain substantial quantities of hydrogen and carbon monoxide, e.g., greater than about 5 mol % each, 10 mol % each, or even 20 mol % of each component. These components will generally be present in the feed and all non-CO₂ product streams, i.e., the recycle methane will always contain some CO and H₂.

[0086] **Fig. 7** is a simplified process flow diagram of a one reactor system **700** for making carbon nanotubes from a gas feed that includes carbon dioxide and methane, in which the methane is in excess. Like numbered items are as discussed in the previous figures, and a portion of the reference numbers have been omitted to simplify the figure. In this embodiment, the feed gas may be higher in methane than in carbon dioxide, for example, at around 80 mol % CH₄ and 20 mol % CO₂, although any ratios may be used. The high methane feed gas **702** can be used in a one reactor system **700** or a two reactor system **800** (**Fig. 8**) to form CNTs. These systems **700** and **800** are similar to those discussed above, except that the gas fractionation system **348** has been replaced with a manifold **704**. When the gas feed **702** is high in methane, the CO₂ may be nearly consumed in the process. Accordingly, there may be no need for further separation.

[0087] In the manifold **704**, the dried gas stream **346** can be separated into portions. A first portion forms the recycle gas **706**, which is blended with the feed gas **702** in a static mixer **306** to form a combined gas stream **308** for feeding the reactor. A second portion may be used as a low BTU fuel gas **528**, for example, feeding a power plant **134** located at the facility. As the dried gas stream **346** includes similar proportions of CH₄, CO, and H₂, in addition to a small amount of CO₂, it will require some purification before it could be sold to a pipeline. Thus, an exported stream **708** of the CH₄ mixture will be limited to other power plants rather than used in consumer applications.

[0088] **Figs. 8A, 8B, and 8C** are simplified process flow diagrams of a two reactor system for making carbon nanotubes from a gas feed that includes carbon dioxide and methane, in which the methane is in excess. Like numbered items are as discussed in previous figures and some reference numbers have been omitted to simplify the figure.

[0089] As the gas feed **702** is higher in methane, the dried gas stream **346** will have a low CO₂ content, making separation uneconomical. Thus, as noted for **Fig. 7**, the gas fractionation system may be replaced with a manifold **704**. The rest of the process will be similar to the system **500** discussed with respect to **Fig. 5**. However, since the CH₄ mixture **708** may be commercially sold to energy markets, a purification system that is configured to generate a much higher purity CH₄, e.g., about 99 mol % CH₄ or higher, may be used.

[0090] It can be understood that the systems for the formation of carbon nanotubes may include any number of reactors, of any number of types, including the fluidized bed reactors shown. In one embodiment, more than two reactors may be used to form the carbon nanotubes.

[0091] Reactor Systems

[0092] **Fig. 9** is a drawing of a fluidized bed reactor **900** for forming carbon nanotubes **902**. A hot gas feed stream **904** is fed through a line **906** into the bottom of the fluidized bed reactor **900**. A control valve **908** may be used to regulate the flow of the hot gas feed stream **904** into the reactor. The hot gas feed stream **904** flows

through a distributor plate **910** and will fluidize a bed of catalyst beads **912** held in place by the reactor walls **914**. As used herein, “fluidize” means that the catalyst beads **912** 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 **914** and heads **915**, as well as the distributor plate **910**, and other parts, can be made of a ceramic material to protect the surfaces.

[0093] As the hot gas feed stream **904** flows through the fluidized bed of catalyst particles **912**, CNTs **902** will form from catalyst beads **912**. The flowing hot gas feed stream **904** carries the CNTs **902** into an overhead line **916** where they are removed from the reactor **900**. Depending on the flow rate, for example, as adjusted by the control valve **908**, some amount of catalyst beads **912**, or particles fragmented from the catalyst beads **912**, may be carried into the overhead line **916**. Accordingly, a catalyst separator **918** may be used to separate catalyst beads **912**, and larger particles, from a reactor effluent stream **920** and return them to the reactor **900** through a recycle line **922**. Any number of configurations may be used for the catalyst separator **918**, including a cyclonic separator, a settling tank, a hopper, and the like. The reactions that take place in the fluidized bed are discussed in more detail in **Fig. 10**.

[0094] **Fig. 10** is a schematic of a catalytic reaction **1000** for the formation of carbon nanotubes on a catalyst bead **1002**. An initial reaction **1004** between a portion of the CH_4 and the CO_2 in the hot gas feed stream **1006** results in the formation of CO and H_2 in stoichiometric amounts. Excess amounts of the source gases **1006** continue to flow through the reactor, helping to fluidize the bed and carrying away CNTs **1008** and catalyst particles **1010**.

[0095] The reactions that form the CNTs **1008** take place on the catalyst bead **1002**. The size of the CNTs **1008**, and the type of CNTs **1008**, e.g., single wall or multiwall

CNTs **1008**, may be controlled by the size of the grains **1012**. In other words, a nucleus of iron atoms of sufficient size at the grain boundary forms the nucleating point for the growth of the carbon products on the catalyst bead **1002**. Generally, smaller grains **1012** will result in fewer layers in the CNTs **1008**, and may be used to obtain single wall CNTs **1008**. Other parameters may be used to affect the morphology of the final product as well, including reaction temperature, pressure, and feed gas flow rates.

[0096] The CO and H₂ react at grain boundaries **1014**, lifting active catalyst particles **1016** off the catalyst bead **1002**, and forming H₂O **1018** and the solid carbon of the CNTs **1008**. The CNTs **1008** break off from the catalyst bead **1002** and from the catalyst particle **1010**. Larger catalyst particles **1010** can be captured and returned to the reactor, for example, by the catalyst separator **918** discussed with respect to **Fig. 9**, while very fine catalyst particles **1010** will be carried out with the CNTs **1008**. The final product will include about 95 mol % solid carbon and about 5 mol % metal, such as iron. The CNTs **1008** will often agglomerate to form clusters **1020**, 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.

[0097] As the reaction proceeds, the catalyst bead **1002** is degraded and finally consumed. Accordingly, the reaction can be described as a metal dusting reaction. 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.

[0098] The catalyst bead **1002** can include any number of other metals, such as nickel, ruthenium, cobalt, molybdenum, and others. However, the catalytic sites on the catalyst beads **1002** are principally composed of iron atoms. In one embodiment, the catalyst bead **1002** includes metal shot, for example, about 25-50 mesh metal beads that are used for shot blasting. In one embodiment, the catalyst may be a stainless ball bearing, and the like.

[0099] Gas Fractionation System

[0100] **Fig. 11** is a simplified process flow diagram of a gas fractionation system **1100** that can be used in a reactor system for the production of carbon nanotubes. The gas fractionation system **1100** is a bulk fractionation process that may be used with a high CO₂ reactor system, such as that discussed with respect to **Fig. 4**. In the gas fractionation system **1100**, the feed gas **1102** is fed to a dryer **1104** to reduce the dew point to about -70 °F (about -56.7 °C), or lower. The feed gas **1102** can correspond to the dried gas stream **366** discussed with respect to **Figs. 3-5**. The dryer **1104** can be a fixed or fluidized dryer bed, containing an adsorbent, such as molecular sieves, desiccants, and the like. Other dryer technologies may also be used, such as cryogenic drier systems. In some embodiments, the dryer can be located prior to the compressor **358**, which may eliminate the need for the ambient temperature heat exchanger **362**.

[0101] The dry gas feed **1106** is then fed through a cryogenic chiller **1108** to reduce the temperature in preparation for the separation. As CO₂ will condense from the gas at about -77 °F (about -61 °C), a multistage chilling system **1110** may be used to reduce the temperature to around this level. The multistage chilling system **1110** may include a heat recovery system **1112** used to heat the outlet gas with energy **1113** from the dry feed gas **1106**.

[0102] The chilled feed **1116** is fed to a separation vessel **1118** to separate a liquid stream **1120** and a vapor stream **1122**. The vapor stream **1122** is passed through an expander **1124** to lower the temperature by generating mechanical work **1126** in an adiabatic expansion process. In one embodiment, the mechanical work **1126** is used to drive a generator **1128**, which may provide a portion of the electricity used in the plant. In another embodiment, the mechanical work **1126** is used to drive a compressor, for example, for compressing a refrigerant stream for the multistage chilling system **1110**. The expansion can result in a two phase stream **1130**.

[0103] The liquid stream **1120** and the two phase stream **1130** are fed to a separation column **1132**, for example, at different points along the separation column

1132. Heat is supplied to the separation column **1132** by a reboiler **1134**. The reboiler **1132** is heated by a stream from a heat exchanger **1136**. The heat exchanger **1136** may be part of a chiller system that is warmer than the separation column **1132**, although below ambient temperature. The column bottom stream **1138** is passed through the reboiler **1134** and a portion **1140** is reinjected after being warmed. An outlet stream **1142** from the reboiler **1134** provides the CO₂ product **1144**. A portion **1146** of the CO₂ product **1144** may be recycled through the heat exchanger **1136** to carry energy to the reboiler **1134**.

[0104] The overhead stream **1148** from the separation column **1132** is a methane enhanced stream, for example, including about 73 mol % CH₄ and about 23 mol % CO₂. As noted, the overhead stream **1148** may be used in a chiller system **1112** to cool the dry gas feed **1106**, warming the overhead stream **1148** to form the recycle gas **1150**. Other components may be present in the recycle gas **1150** including, for example, about 3.5 mol % CO and H₂. If the methane is intended for sale, such as in the high methane reaction system discussed with respect to **Fig. 9**, a higher purity separation system may be used, as discussed with respect to **Fig. 9**.

[0105] The configurations and units discussed with respect to **Figs. 11** are merely exemplary. Any number of variations may be made to these systems. Further, other gas separation systems may be used in embodiments, so long as flow rates and purity levels can be achieved.

[0106] Packaging System

[0107] **Fig. 12** is a simplified process flow diagram of a packaging system **1200** that can package carbon nanotubes separated from an effluent stream from a one reactor system. The packaging system **1200** overlaps the lock hopper **522** of the separations systems **518** and **632** shown in **Figs. 5** and **6**, and is used to isolate the CNTs from the process for packaging.

[0108] The packaging system **1200** is part of a packaging train **1202**. The packaging train **1202** may have a sampling valve **1204** to remove CNTs from the lock hopper **522**.

The sampling valve **1204** 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 **1204** may be a ball valve configured to open 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 **1206** for purging and cooling.

[0109] After the sampling valve **1204** has closed, a purge stream **1208** may be opened into the drum **1206** to sweep out remaining gases, such as CO, H₂, H₂O, and CH₄. As noted, the purge stream **1208** 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 **1210** will carry some amount of CNTs, and other fine particles, and may be passed through a filter **1212**, prior to being sent back to the process as a purge return **1214**. The filter **1212** may be a bag filter, cyclonic separator, or any other suitable separation system. After purging is completed, a packaging valve **1216** will open to allow a stream **1218** including CNTs to flow to a filling station **1220** to be packaged in drums or tanks for sale.

[0110] **Fig. 13** is a simplified process flow diagram of a separation system **1300** that can package carbon nanotubes separated from each reactor effluent stream in a two reactor system. As shown in **Fig. 13**, in a two reactor system, such as discussed with respect to **Figs. 7** and **8**, each reactor in the system may have a separate packaging train, such as packaging trains **1202** and **1302**. The first packaging train **1202** may be coupled to lock hopper **522** of separation system **518**, while the second packaging train **1302** may be coupled to the lock hopper **522** of separation system **632**. As the different reactors may be producing different amounts of CNTs, the equipment may be sized differently, although the functions may be the same. For example, in the first simulation, the amount of CNTs isolated by the first packaging train **1202** may be about 162.7 tons/day (148,000 kg/day), while the amount removed to the second packaging train **1302** may be about 57.5 tons/day (52,000 kg/day).

[0111] The isolation system described above is merely exemplary. Any number of other systems may be used in embodiments. However, the CNTs have a very low density, of less than about 0.5 g/cc, depending on morphological distribution, and may best be packaged in a system configured to isolate them from the atmosphere to lower the amount lost to the plant environment. Further, the purge gas may be isolated from the feed gases, as shown for the systems in **Figs. 5** and **6**, or may be separately provided, for example, for the systems in **Figs. 7** and **8**.

[0112] Method

[0113] **Fig. 14** is a method **1400** for generating carbon nanotubes from a feed gas that includes methane and carbon dioxide. The method **1400** begins at block **1402**, at which a mixed CO₂ / CH₄ feedstock 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 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.

[0114] At block **1404**, the feedstock is combined with a recycle gas obtained from the wastes gases generated in the process. As described herein, the recycle gas may be obtained from the waste gases by cryogenic gas fractionation, as well as any number of other techniques. At block **1406**, the combined gas stream is heated with waste heat recovered from the reaction process. After heating, at block **1408**, the combined gas stream is reacted with a metal catalyst in a reactor to form the CNTs. At block **1410**, the CNTs are separated from the waste gas. At block **1412**, the separated CNTs are purged, cooled, and packaged to be sent to market.

[0115] The waste gas is cooled to remove excess water formed 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. The processes described at blocks **1406-1414** will be repeated for each sequential reactor in the reaction system.

[0116] At block **1416**, the waste gas is fractionated into a CO₂ enriched stream and a CH₄ enriched stream. At block **1418**, whichever stream contains the excess reagent can be sold, while the other stream can be recycled to block **1404** to be used in the process.

[0117] Still other embodiments of the claimed subject matter may include any combinations of the elements listed in the following numbered paragraphs:

1. A system for the production of carbon nanotubes, comprising:
a feed gas heater configured to heat a feed gas with waste heat from a waste gas stream;
a reactor configured to form carbon nanotubes from the feed gas in a Bosch reaction;
a separator configured to separate the carbon nanotubes from a reactor effluent stream forming the waste gas stream; and
a water removal system, comprising an ambient temperature heat exchanger and a separator configured to separate a bulk of water from the waste gas stream to form a dry waste gas stream.
2. The system of paragraph 1, wherein the ambient temperature heat exchanger comprises a water chiller.
3. The system of paragraphs 1 or 2, wherein the ambient temperature heat exchanger comprises an air cooled heat exchanger.
4. The system of paragraphs 1, 2 or 3, comprising a package heater configured to heat the feed gas for an initial startup of the system.
5. The system of any of the preceding paragraphs, comprising:
a compressor configured to increase the pressure of the dry waste gas stream;
and

a final water removal system configured to remove water from the dry waste gas stream.

6. The system of paragraph 5, comprising a gas fractionation system configured to separate a methane rich stream and a CO₂ rich stream from the dry waste gas stream.

7. The system of paragraph 6, comprising a mixing system configured to mix the methane rich stream into the feed gas before the feed gas heater.

8. The system of any of paragraphs 1-5, wherein the reactor is a fluidized bed reactor using a counter-current flow of feed gas to fluidize a catalyst.

9. The system of paragraph 8, wherein the catalyst comprises metal shot-blasting beads.

10. The system of any of paragraphs 1-5, or 8, comprising:

a heat exchanger configured to heat the dry waste gas stream with waste heat from the waste gas stream to form a second feed gas;

a second reactor configured to form carbon nanotubes from the second feed gas;

a separator configured to separate the carbon nanotubes from an effluent stream from the second reactor forming a second waste gas stream, and wherein the waste gas stream used in the feed gas heater comprises the second waste gas stream; and

a water removal system configured to separate water from the second waste gas stream using an ambient temperature heat exchanger to chill the second waste gas stream and remove the bulk of the water to form a second dry waste gas stream.

11. The system of paragraph 10, comprising:

a compressor configured to increase a pressure of the second dry waste gas stream; and

a final water removal system configured to remove water from the second waste gas stream.

12. The system of paragraph 11, comprising a gas fractionation system configured to separate a methane rich stream and a CO₂ rich stream from the second waste gas stream.

13. The system of paragraph 12, comprising a mixing system configured to mix the methane rich stream into the feed gas before the feed gas heater.

14. The system of any of paragraphs 1-5, 8, or 10, wherein the reactor is a fluidized bed reactor using a counter-current flow of feed gas to fluidize a catalyst.

15. The system of paragraph 14, wherein the catalyst comprises metal shot-blasting beads.

16. The system of paragraph 14, wherein the catalyst comprises metal beads comprising iron and nickel, chromium, or any combinations thereof.

17. The system of paragraph 14, wherein the catalyst comprises metal beads between about 25 mesh and 50 mesh in size.

18. The system of any of paragraphs 1-5, 8, 10, or 14, wherein the reactor is lined with a material configured to prevent degradation of a metal shell.

19. The system of any of paragraphs 1-5, 8, 10, 14, or 18, wherein a piping connection between the reactor and a cross heat exchanger is lined with a refractory material configured to protect a metal surface from degradation.

20. The system of any of paragraphs 1-5, 8, 10, 14, 18, or 19, wherein the feed gas heater comprises a heat exchanger configured for use in a metal dusting environment.

21. A method for forming carbon nanotubes, comprising:
forming carbon nanotubes in a reactor using a Bosch reaction;
separating the carbon nanotubes from a reactor effluent to form a waste gas stream;
heating the feed gas, a dry waste gas stream, or both, with waste heat from the waste gas stream; and

chilling the waste gas stream in an ambient temperature heat exchanger to
condense water vapor, forming the dry waste gas stream.

22. The method of paragraph 21, comprising:
compressing the dry waste gas stream to form a compressed gas;
passing the compressed gas through an ambient temperature heat exchanger to
condense and remove any remaining water vapor;
fractionating the compressed gas to separate methane and carbon dioxide; and
adding the methane to the feed gas.

23. The method of paragraphs 21 or 22, comprising:
feeding the dry waste gas stream to a second reactor;
forming another portion of carbon nanotubes in the second reactor;
separating the carbon nanotubes to form a second waste gas stream;
heating the feed with waste heat from the second waste gas stream; and
chilling the second waste gas stream in an ambient temperature heat exchanger
to condense water vapor, forming a second dry waste gas stream.

24. The method of any of paragraphs 21-23, comprising:
compressing the second dry waste gas stream to form a compressed gas;
passing the compressed gas through an ambient temperature heat exchanger to
condense and remove any remaining water vapor;
fractionating the compressed gas to separate methane and carbon dioxide; and
adding the methane to the feed gas.

25. A reaction system for forming carbon nanotubes, comprising:
two or more reactors configured to form carbon nanotubes from gas streams
using a Bosch reaction, wherein an effluent from each reactor, before a
final reactor, is used as a feed stream for a downstream reactor, and
wherein an effluent stream from the final reactor comprises a reactant
depleted waste stream;

- a separation system downstream of each reactor, wherein the separation system is configured to remove carbon nanotubes from the effluent from the reactor;
- a feed heater downstream of each separation system, wherein the feed heater comprises a heat exchanger configured to heat a feed gas stream for a following reactor using waste heat from the effluent from the reactor, and wherein the feed heater downstream of the final reactor is configured to heat a gas stream for the first reactor;
- an ambient temperature heat exchanger downstream of each feed heater, wherein the ambient temperature heat exchanger is configured to remove water from the effluent, forming the feed stream for the following reactor;
- a compressor configured to increase the pressure of the reactant depleted waste stream;
- an ambient temperature heat exchanger downstream of the compressor, configured to remove water from the reactant depleted waste stream;
- a gas fractionation system configured to separate the reactant depleted waste stream into a methane enriched stream and a carbon dioxide enriched stream; and
- a mixer configured to blend the methane enriched stream or the carbon dioxide enriched stream into an initial feed stream.

26. The reaction system of paragraph 25, wherein a reactor comprises a fluidized bed reactor using metal beads as a catalyst.

27. The reaction system of paragraphs 25 or 26, comprising a separation vessel downstream of each of the ambient temperature heat exchangers, wherein the separation vessel is configured to separate liquid water from a gas stream.

28. The reaction system of any of paragraphs 25-27, comprising a plurality of package heaters configured to heat the feed stream to the each of the two or more reactors.

29. The reaction system of any of paragraphs 25-28, comprising a package heater configured to heat an initial feed stream for plant startup.

30. The reaction system of paragraph 29, wherein the package heater is used to heat a feed stream to a subsequent reactor.

31. The reaction system of paragraph 29, wherein the package heater is a heater configured to be field erected, or an electric power heater, a commercial heater configured for heating gases, or any combinations thereof.

32. The reaction system of paragraph 29, wherein the package heater is configured to heat a reducing gas stream without substantial damage.

[0118] 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 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 the production of carbon nanotubes, comprising:
a feed gas heater configured to heat a feed gas with waste heat from a waste gas stream;
a reactor configured to form carbon nanotubes from the feed gas in a Bosch reaction;
a separator configured to separate the carbon nanotubes from a reactor effluent stream forming the waste gas stream; and
a water removal system, comprising an ambient temperature heat exchanger and a separator configured to separate a bulk of water from the waste gas stream to form a dry waste gas stream.
2. The system of claim 1, wherein the ambient temperature heat exchanger comprises a water chiller.
3. The system of claim 1, wherein the ambient temperature heat exchanger comprises an air cooled heat exchanger.
4. The system of claim 1, comprising a package heater configured to heat the feed gas for an initial startup of the system.
5. The system of claim 1, comprising:
a compressor configured to increase the pressure of the dry waste gas stream;
and
a final water removal system configured to remove water from the dry waste gas stream.

6. The system of claim 5, comprising a gas fractionation system configured to separate a methane rich stream and a CO₂ rich stream from the dry waste gas stream.
7. The system of claim 6, comprising a mixing system configured to mix the methane rich stream into the feed gas before the feed gas heater.
8. The system of claim 1, wherein the reactor is a fluidized bed reactor using a counter-current flow of feed gas to fluidize a catalyst.
9. The system of claim 8, wherein the catalyst comprises metal shot-blasting beads.
10. The system of claim 1, comprising:
 - a heat exchanger configured to heat the dry waste gas stream with waste heat from the waste gas stream to form a second feed gas;
 - a second reactor configured to form carbon nanotubes from the second feed gas;
 - a separator configured to separate the carbon nanotubes from an effluent stream from the second reactor forming a second waste gas stream, and wherein the waste gas stream used in the feed gas heater comprises the second waste gas stream; and
 - a water removal system configured to separate water from the second waste gas stream using an ambient temperature heat exchanger to chill the second waste gas stream and remove the bulk of the water to form a second dry waste gas stream.

11. The system of claim 10, comprising:
a compressor configured to increase a pressure of the second dry waste gas stream; and
a final water removal system configured to remove water from the second waste gas stream.
12. The system of claim 11, comprising a gas fractionation system configured to separate a methane rich stream and a CO₂ rich stream from the second waste gas stream.
13. The system of claim 12, comprising a mixing system configured to mix the methane rich stream into the feed gas before the feed gas heater.
14. The system of claim 1, wherein the reactor is a fluidized bed reactor using a counter-current flow of feed gas to fluidize a catalyst.
15. The system of claim 14, wherein the catalyst comprises metal shot-blasting beads.
16. The system of claim 14, wherein the catalyst comprises metal beads comprising iron and nickel, chromium, or any combinations thereof.
17. The system of claim 14, wherein the catalyst comprises metal beads between about 25 mesh and 50 mesh in size.
18. The system of claim 1, wherein the reactor is lined with a material configured to prevent degradation of a metal shell.

19. The system of claim 1, wherein a piping connection between the reactor and a cross heat exchanger is lined with a refractory material configured to protect a metal surface from degradation.

20. The system of claim 1, wherein the feed gas heater comprises a heat exchanger configured for use in a metal dusting environment.

21. A method for forming carbon nanotubes, comprising:
forming carbon nanotubes in a reactor using a Bosch reaction;
separating the carbon nanotubes from a reactor effluent to form a waste gas stream;
heating a feed gas, a dry waste gas stream, or both, with waste heat from the waste gas stream; and
chilling the waste gas stream in an ambient temperature heat exchanger to condense water vapor, forming the dry waste gas stream.

22. The method of claim 21, comprising:
compressing the dry waste gas stream to form a compressed gas;
passing the compressed gas through an ambient temperature heat exchanger to condense and remove any remaining water vapor;
fractionating the compressed gas to separate methane and carbon dioxide; and
adding the methane to the feed gas.

23. The method of claim 21, comprising:
feeding the dry waste gas stream to a second reactor;
forming another portion of carbon nanotubes in the second reactor;
separating the carbon nanotubes to form a second waste gas stream;
heating the feed with waste heat from the second waste gas stream; and

chilling the second waste gas stream in an ambient temperature heat exchanger to condense water vapor, forming a second dry waste gas stream.

24. The method of claim 23, comprising:
compressing the second waste gas stream to form a compressed gas;
passing the compressed gas through an ambient temperature heat exchanger to condense and remove any remaining water vapor;
fractionating the compressed gas to separate methane and carbon dioxide; and
adding the methane to the feed gas.

25. A reaction system for forming carbon nanotubes, comprising:
two or more reactors configured to form carbon nanotubes from gas streams using a Bosch reaction, wherein an effluent from each reactor, before a final reactor, is used as a feed stream for a downstream reactor, and wherein an effluent stream from the final reactor comprises a reactant depleted waste stream;
a separation system downstream of each reactor, wherein the separation system is configured to remove carbon nanotubes from the effluent from the reactor;
a feed heater downstream of each separation system, wherein the feed heater comprises a heat exchanger configured to heat a feed gas stream for a following reactor using waste heat from the effluent from the reactor, and wherein the feed heater downstream of the final reactor is configured to heat a gas stream for the first reactor;
an ambient temperature heat exchanger downstream of each feed heater, wherein the ambient temperature heat exchanger is configured to remove water from the effluent, forming the feed stream for the following reactor;

a compressor configured to increase the pressure of the reactant depleted waste stream;

an ambient temperature heat exchanger downstream of the compressor, configured to remove water from the reactant depleted waste stream;

a gas fractionation system configured to separate the reactant depleted waste stream into a methane enriched stream and a carbon dioxide enriched stream; and

a mixer configured to blend the methane enriched stream or the carbon dioxide enriched stream into an initial feed stream.

26. The reaction system of claim 25, wherein a reactor comprises a fluidized bed reactor using metal beads as a catalyst.

27. The reaction system of claim 25, comprising a separation vessel downstream of each of the ambient temperature heat exchangers, wherein the separation vessel is configured to separate liquid water from a gas stream.

28. The reaction system of claim 25, comprising a plurality of package heaters configured to heat the feed stream to the each of the two or more reactors.

29. The reaction system of claim 25, comprising a package heater configured to heat an initial feed stream for plant startup.

30. The reaction system of claim 29, wherein the package heater is used to heat a feed stream to a subsequent reactor.

31. The reaction system of claim 29, wherein the package heater is a heater configured to be field erected, or an electric power heater, a commercial heater configured for heating gases, or any combinations thereof.

32. The reaction system of claim 29, wherein the package heater is configured to heat a reducing gas stream without substantial damage.