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(54) Title: REACTOR SYSTEM FOR THE PRODUCTION OF CARBON ALLOTROPES

(57) Abstract: Systems and a method for forming carbon allotropes are described. An exemplary reactor system for the production of carbon allotropes includes a hybrid reactor configured to form carbon allotropes from a reactant gas mixture in a Bosch reaction. The hybrid reactor includes at least two distinct zones that perform different functions including reaction, attrition, catalyst separation, or gas separation.

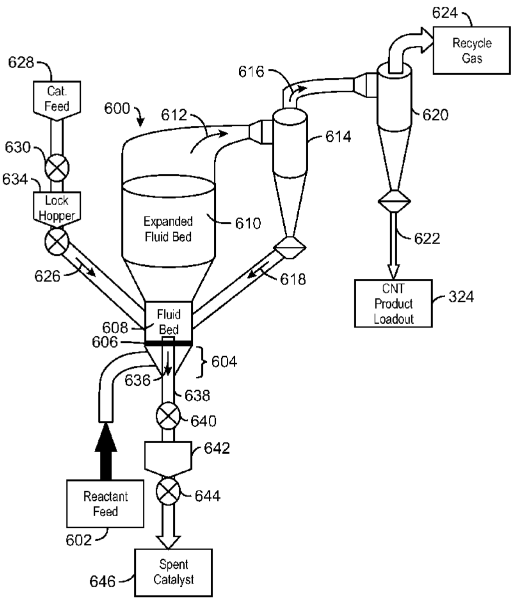

FIG. 6

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REACTOR SYSTEM FOR THE PRODUCTION OF CARBON ALLOTROPES

FIELD

[0001] The present techniques relate to an industrial scale process for forming carbon fibers and carbon nanomaterials.

BACKGROUND

[0002] 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.

[0003] Materials formed predominately of solid or elemental carbon, i.e., carbon allotropes, 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.

[0004] More recently developed carbon allotropes, such as fullerenes, are starting to be used 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 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.

[0005] 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.

[0006] 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.

[0007] 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/C_2H_2 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.

[0008] International Patent Application Publication No. 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.

[0009] While all of the techniques described can be used to form carbon allotropes, 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

[0010] An embodiment described herein provides a reactor system for the production of carbon allotropes. The reactor system includes a hybrid reactor configured to form carbon allotropes from a reactant gas mixture in a Bosch reaction. The hybrid reactor includes at least two distinct zones that perform different functions including reaction, attrition, catalyst separation, or gas separation.

[0011] Another embodiment provides a method for forming carbon allotropes. The method includes injecting a reactant gas into a hybrid reactor, wherein the hybrid reactor includes at least two zones, and wherein each zone performs a function including reaction, catalyst separation, attrition, or gas separation. The reactant gas includes a carbon oxide and a hydrocarbon. Carbon allotropes are formed in the hybrid reactor using a Bosch reaction. Catalyst particles are separated from the reactant gas to form a waste gas stream and the carbon allotropes are separated from the waste gas stream.

[0012] Another embodiment provides a reaction system for forming carbon allotropes. The reaction system includes a hybrid reactor configured to form carbon allotropes from gas streams using a Bosch reaction, wherein the hybrid reactor includes at least two distinct functional zones. Each zone is configured to perform a function including reaction, attrition, catalyst separation, or gas separation. A separation system downstream of the hybrid reactor is configured to remove carbon allotropes from an effluent from the hybrid reactor. A feed heater is located downstream of the separation system, wherein the feed heater includes a heat exchanger configured to heat a feed gas stream for the hybrid reactor using waste heat from the effluent from the hybrid reactor. A heat exchanger is located downstream of the separation system, wherein the heat exchanger is configured to remove water from the effluent. A gas separation 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

[0013] The advantages of the present techniques are better understood by referring to the following detailed description and the attached drawings, in which:

[0014] **Fig. 1A** is a block diagram of a reaction system that generates carbon allotropes, for example, as a by-product of a carbon dioxide sequestration reaction;

[0015] **Fig. 1B** is a block diagram of the use of an excess carbon dioxide feed in an enhanced oil recovery (EOR) process;

[0016] **Fig. 1C** is a block diagram of the use of an excess methane feed in a power generation process;

[0017] **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;

[0018] **Fig. 3** is a simplified process flow diagram of a reactor system for making carbon allotropes from a gas feed that includes carbon dioxide and methane;

[0019] **Fig. 4** is a simplified process flow diagram of another reactor system for making carbon allotropes from a gas feed that includes carbon dioxide and methane;

[0020] **Fig. 5** is a drawing of a reactor for forming carbon allotropes;

[0021] **Fig. 6** is a drawing of a hybrid fluidized bed reactor for forming carbon allotropes;

[0022] **Fig. 7** is a drawing of another hybrid fluidized bed reactor for forming carbon allotropes;

[0023] **Fig. 8** is a drawing of a hybrid packed bed reactor for forming carbon allotropes;

[0024] **Fig. 9** is a drawing of a hybrid spouted bed reactor for forming carbon allotropes;

[0025] **Fig. 10** is a drawing of hybrid packed/fluidized bed reactor for forming carbon allotropes;

[0026] **Fig. 11** is a drawing of a two hybrid reactor system for forming carbon allotropes;

[0027] **Fig. 12** is a schematic of a catalytic reaction for the formation of carbon allotropes on a catalyst bead;

[0028] **Fig. 13** is a simplified process flow diagram of a gas separation process that can be used to separate excess carbon dioxide from a recycle gas in a reactor system for the production of carbon allotropes;

[0029] **Fig. 14** is a simplified process flow diagram of a packaging system that can package carbon allotropes separated from a reactor effluent stream from a one reactor system; and

[0030] **Fig. 15** is a method for generating carbon allotropes 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 allotropes” as used herein and in the claims, includes carbon fibers, carbon nanofibers, carbon nanotubes, other carbon nanostructures, and other allotropes of carbon.

[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 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.

[0039] Overview

[0040] Embodiments described herein provide hybrid reactor systems 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. As used herein, a hybrid reactor includes one or more distinct zones, in which each zone performs a specific function, such as reaction, attrition, catalyst separation, or gas separation, or any combinations thereof. The hybrid reactors may include various combinations of packed beds, fluidized beds, and transport reactors. Further, the hybrid reactor systems may include multiple reactors in staged configurations. The hybrid reactor systems described herein can efficiently produce carbon allotropes, attrit carbon allotropes from catalyst particles, eliminate the need for downstream separation equipment to return catalyst particles to the reactor, and the like.

[0041] In some embodiments, feedstocks that are higher in CH_4 may be used, while in other embodiments, feedstocks used are higher in CO_2. Other feedstocks may be used, including mixtures of H_2, CO, CO_2, and other hydrocarbons. The process is conducted under high temperature and pressure conditions using a Bosch reaction, as discussed with respect to **Fig. 2**.

[0042] 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 separation system is used to separate any remaining amounts of the limiting reagent from a waste gas mixture and recycle this reagent to the process.

[0043] Embodiments described herein can be used to produce industrial quantities of carbon allotropes 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. The reactor designs discussed with respect to **Figs. 6-11** will allow large scale production of carbon allotropes allowing large quantities to be produced. The large scale production can provide a more consistent product.

[0044] **Fig. 1A** 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 a feed gas **102**, which can be a mixture of CO_2 and CH_4. In some embodiments, the reaction may allow for sequestration of CO_2 from exhaust streams of power plants and the like. In other embodiments, the CH_4 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 C_2H_6, C_2H_4, and the like. In one embodiment, the feed gas **102** has been treated to remove these components, for example, for sale as product streams.

[0045] 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 an appropriate reaction temperature, e.g., about 500-1200 ºC (about 930-2192 ºF). In one embodiment, the feed is heated to between about 600 ºC (about 1112 ºF) and about 1050 ºC (about 1742 ºF). In another embodiment, the feed is heated to between about 850 ºC (about 1562 ºF) and about 950 ºC (about 1742 ºF). In another embodiment, the feed is heated to between about 890 ºC (about 1634 ºF) and about 910 ºC (about 1742 ºF). The heated feed gas **108** is fed to a hybrid reactor **110**.

[0046] In the hybrid reactor **110**, a catalyst reacts with a portion of the heated feed gas **108** to form carbon allotropes **112** using the Bosch reaction. As described in more detail below, the hybrid reactor **110** can include multiple functional zones, optimized for reaction, attrition, catalyst separation, gas separation, and the like. Any number of different catalysts may be used, including, for example, metal shot, supported catalysts, and the like. The carbon allotropes **112** are separated from the flow stream **114** out of the hybrid 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**.

[0047] 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 separation 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 **122** may be greater than about -5 ºC (about 23 ºF), greater than about 0 ºC (about 32 ºF), greater than about 5 ºC (about 41 ºF), greater than about 10 ºC (about 50 ºF), greater than about 20 ºC (about 68 ºF), or higher. A dryer may be used to lower the dewpoint, for example, to about -50 ºC (about -58 ºF), about -70 ºC (about -94 ºF), or lower, prior to gas separation.

[0048] The gas separation 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 CO_2 is the highest concentration gas in a blend with CH_4, the gas separation system **124** can be used to remove CH_4 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 separation system **124** may not be needed when the CH_4 is in excess, as much of the CO_2 may be consumed in the reaction. Thus, the excess feed **128** that contains the CH_4, and which may also contain H_2, 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**.

[0049] **Fig. 1B** 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 CO_2, the excess feed **128** may be sold to a distributor for marketing through a pipeline **130**. Individual users may obtain the CO_2 from the pipeline **130** and use it in enhanced oil recovery processes **132**. For example, the CO_2 can be used to pressurize hydrocarbon reservoirs to increase the recovery of hydrocarbons.

[0050] **Fig. 1C** 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 CH_4, 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 formation of the carbon allotropes, and, thus, the excess feed **128** may be purified prior to any commercial sales, such as to a pipeline company. Further, the excess feed may be used in a liquefaction process to form liquefied natural gas (LNG) for sale.

[0051] **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.

[0052] 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.

[0053] 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 types of carbon allotropes. 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 carbon allotropes, such as CNTs.

[0054] Reaction Systems

[0055] **Fig. 3** is a simplified process flow diagram of a reactor system **300** for making carbon allotropes 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 CO_2 or higher in CH_4. 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**.

[0056] 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 ºC (930 ºF), about 750 ºC (about 1382 ºF), about 850 ºC (about 1562 ºF), about 950 ºC (about 1742 ºF), about 1050 ºC (about 1742 ºF), or about 1200 ºC (about 2192 ºF) 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 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 hybrid reactor **318**. Hybrid reactor designs that may be used are discussed with respect to **Figs. 6** through **11**.

[0057] The carbon allotropes are carried from the hybrid reactor **318** in a reactor effluent stream **320**. The reactor effluent stream **320** may be at an elevated temperature, for example, about 600 ºC (about 1112 ºF), about 1050 ºC (about 1742 ºF), or about 1200 ºC (about 2192 ºF) , 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 allotropes **324**. The resulting waste gas stream **326** can used to provide heat to the combined gas stream **308** in the heat exchanger **310**. The carbon allotropes may also be removed in secondary separation devices (not shown) at lower temperatures than the waste gas stream **326**.

[0058] 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 ºC (about 86 ºF), about 38 ºC (about 100 ºF), about

40 ºC (about 104 ºF) and at a pressure of about 2500 kilopascals (kPa) (about 363 psia), about 3000 kPa (about 425 psia), about 3720 kPa (about 540 psia), or about 4000 kPa (about 580 psia). Operations are not limited to ambient temperature cooling, as in some embodiments it may be desirable to use sub-ambient cooling systems. For example, the heat exchanger may use a glycol/water based stream in the heat exchanger **330.** 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 725 psia), about 6000 kPa (about 870 psia), about 7000 kPa (about 1015 psia), about 7,240 kPa (about 1050 psia), or about 8000 kPa (about 1160 psia), 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.

[0059] In embodiments in which the CO_2 is in excess in the feed gas **302**, the dried gas stream **346** is then sent to a gas separation system **348**, which separates the excess feed **350** from the recycle gas **304**. In reaction systems **300** based on a proportionate excess of CO_2, the excess feed **350** may primarily include CO_2 and the recycle gas **304** may primarily include CH_4. In reaction systems **300** based on a proportionate excess of CH_4, the excess feed **350** will not have a substantial CO_2 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.

[0060] The reaction conditions used can cause significant degradation of metal surfaces, as indicated by choice of the catalyst itself, which may include carbon steel beads, stainless steel beads, or any number of other materials, as discussed herein. 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.

[0061] **Fig. 4** is a simplified process flow diagram of another reactor system **400** for making carbon allotropes from a gas feed that includes carbon dioxide and methane. In **Fig. 4**, 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 **402**. The main difference between the more detailed process flow diagram of **Fig. 4** and that of **Fig. 3** is the use of heat exchangers to cool the reactor effluent stream **320** prior to separating the carbon allotropes from the reactor effluent stream **320**.

[0062] In this embodiment, the heated gas stream **312** is raised to a temperature of about 300 ºC (about 572 ºF), about 400 ºC (about 752 ºF), about 427 ºC (about 800 ºF), or about 500 ºC (about 932 ºF) in the heat exchanger **310** prior to flowing through a second heat exchanger **404**. In the second heat exchanger **404**, the heated gas stream **312** flows through a first ceramic block heat exchanger **406**, as indicated by arrows **408**. Heat stored in the first ceramic block heat exchanger **406** is exchanged to the heated gas stream **312** and may increase the temperature to about 500 ºC (930 ºF), about 750 ºC (about 1382 ºF), about 850 ºC (about 1562 ºF), about 950 ºC (about 1742 ºF), about 1050 ºC (about 1742 ºF), or about 1200 ºC (about 2192 ºF).

[0063] While the first ceramic block heat exchanger **406** is used to heat the heated gas stream **312**, a second ceramic block heater **410** is used to cool the reactor effluent stream **320** by flowing this stream through the second ceramic block heater **410**, as indicated by arrows **412**. When the second ceramic block heat exchanger **410** reaches a selected temperature, or the first ceramic block heat exchanger **406** drops to a selected temperature, the positions of the inlet valves **414** and outlet valves **416** 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 **406** or **410** is being heated by the flow from the reactor **318** and which ceramic block heat exchanger **406** or **410** is used to heat the heated gas stream **312**. The valves are not limited to the configuration shown, as the inlet valves **414** and outlet valves **416** may be replaced with three way valves in some embodiments.

[0064] The heat may not be sufficient to increase the temperature sufficiently for reaction. Thus, as described with respect to **Fig. 3**, a 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 hybrid reactor **318**. Carbon allotropes, such as carbon nanotubes, are formed in the hybrid reactor **318**, and carried out in the reactor effluent stream **320**.

[0065] After flowing through the second ceramic block heater **410,** the reactor effluent **320** is flowed to a separation system **418**, which is used to remove the carbon allotropes **324** from the reactor effluent **320**. In this embodiment, the separation system **418** for the carbon allotropes includes a cyclonic separator **420**, a lock hopper **422**, and a filter **424**. In an embodiment, the cyclonic separator **420** and the lock hopper **422** may be placed upstream of the ceramic block heaters **406** and **410**. After the majority of the carbon allotropes are removed by the cyclonic separator **420** and deposited into the lock hopper **422**, the filter **424** is used to remove remaining carbon allotropes from the waste gas stream **426**. This may help to prevent plugging, or other problems, caused by residual carbon allotropes in the waste gas stream **426**. The filter **424** can include bag filters, sintered metal filters, and ceramic filters, among other types. From the separation systems **418**, the carbon allotropes may be directed to a packaging system, as discussed in further detail with respect to **Fig. 14**. After the filter **424**, the waste gas stream **426** 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**.

[0066] In this embodiment, two extra streams may be provided from the separated streams out of the gas separation system **348**. A fuel gas stream **428** 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 **430** may be taken from the CO_2 outlet stream, which can be used to purge various pieces of equipment, such as the filter **424** or cyclone **420**.

[0067] Reactor Systems

[0068] **Fig. 5** is a drawing of a reactor **500** for forming carbon allotropes **502**. A hot gas feed stream **504** is fed through a line **506** into the bottom of the reactor **500**. A control valve **508** may be used to regulate the flow of the hot gas feed stream **504** into the reactor **500**. The hot gas feed stream **504** flows through a distributor plate **510** and will fluidize a bed of catalyst beads **512** held in place by the reactor walls **514**. As used herein, “fluidize” means that the catalyst beads **512** 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 **514** and heads **515**, as well as the distributor plate **510**, and other parts, can be made of a ceramic material to protect the surfaces.

[0069] As the hot gas feed stream **504** flows through the fluidized bed of catalyst particles **512**, carbon allotropes **502** will form from catalyst beads **512**. The flowing hot gas feed stream **504** carries the carbon allotropes **502** into an overhead line **516** where they are removed from the reactor **500**. Depending on the flow rate, for example, as adjusted by the control valve **508**, some amount of catalyst beads **512**, or particles fragmented from the catalyst beads **512**, may be carried into the overhead line **516**. Accordingly, a catalyst separator **518** may be used to separate catalyst beads **512**, and larger particles, from a reactor effluent stream **520** and return them to the reactor **500** through a recycle line **522**. Any number of configurations may be used for the catalyst separator **518**, including a cyclonic separator, a settling tank, a hopper, and the like. Further, any number of reactor designs can be used. A separate catalyst separator **518** may not be needed in various designs, as a separation zone may be included in a hybrid reactor design.

[0070] The reactor design must balance various phenomena to be effective. Each of these phenomena has a different time scale that must be managed simultaneously by the reactor concept. The reactor phenomena and corresponding timescales are summarized in Table 1 for the production of carbon nanotubes. The growth time scales may be somewhat different for other types of carbon allotropes.

[0071] Table 1 Reactor Phenomena and Their Time Scales

Phenomenon	**Time Scale**
Reaction	~100 seconds (s)
Gas Flow	~1 s
CNT growth	~250 s
CNT attrition	~10 s
CNT freeboard growth	~40 s
Catalyst Loss	~20,000 s

[0072] These phenomena, each with their unique time scale, control the reactor design. The first phenomenon is that of the catalytic chemical reaction, itself. As discussed herein, various metals, intermetallics, and supported metal catalysts are potential catalytic materials for this reaction. At the operating conditions of the reactor, which can include various pressures and temperatures, the reaction has a time scale on the order of minutes. For example, the pressures that may be involved are between about 0.1 KPa (about 0.015 psia) and about 7000 KPa (about 1015 psia), between about 3000 KPa (about 435 psia) to about 5000 KPa (about 725 psia), or between about 3500 KPa (about 508 psia) to about 4500 KPa (about 653 psia). The temperatures of the reaction may be in the range of between about 800 ºC (about 1472 ºF) and about 1050 ºC (about 1922 ºF), or about 850 ºC (about 1562 ºF) to about 950 ºC (about 1742 ºF).

[0073] Another phenomenon is that of the gas flow in the reactor. Due to the use of a catalyst the gas passes through the reactor quickly, on the order of seconds. In this time frame the reaction conversion should be 10 % to 20 % on a single pass basis for CNTs to be economically produced.

[0074] Another phenomenon is the growth of CNTs to a particular length. Assuming that the average length is 100 microns, the growth time may be about four minutes. However, this time may be cut short by the attrition of the CNTs from the catalyst surfaces, e.g., catalyst particles, within the reactor bed. The time scale for carbon nanotube attrition may be between about 10 s and about 3600 s. In addition, the growth time may be extended by the time that the gas passes through the reactor (on the order of one second).

[0075] The growth time may also be extended by the time for gas to pass through the freeboard of the reactor, and any additional piping, before a cyclone separator removes the carbon allotropes from the hot reactant gases. Freeboard CNT growth is growth that continues on catalyst particles that are in the predominantly gas-filled volume above the fluidized bed. This volume is commonly referred to as the freeboard in the art. The catalyst particles can be in the form of distinct catalyst particles of micro-scale (~1 micron and larger) or in the form of catalyst nano-scale particles (~10-1000 nanometers) to which typically one or more carbon nanotubes are attached. The time in the freeboard may be controlled by the design of the reactor and may be as long as 40 seconds (s). As used herein, the freeboard is the head space in the reactor above a reaction bed.

[0076] It can be noted that the catalyst is consumed very slowly during the course of the reaction. As a result, another phenomenon is the catalyst consumption. Assuming 400 micron (0.4 mm) steel grit as the catalyst, the average catalyst removal time is on the order of 55 hours. It can also be noted that the steel grit catalyst needs to be reduced so that the surface does not have an oxide layer, before it is an effective catalyst. The reduction of the catalyst is typically done during start up and is not an important time scale for the steady state operation of the reactor. However, having a short catalyst reduction time is also an important advantage. Shorter reduction times occur with larger catalyst particles that have smaller specific surface areas. Any reactor design must manage these phenomena and their associated time scales to be an appropriate design for this reaction.

[0077] Further, at the operating conditions used, metal dusting corrosion is significant unless high alloy steels are used, including, for example, Inconel 693, Inconel 696, and others with high chromium equivalent content, e.g., greater than 24 %. The reactors may be designed with refractory lined carbon steel vessels allowing the steel walls to be kept cool and protected from the reactions, minimizing corrosion and erosion. **Figs. 6-11** show various reactor designs that may be used in embodiments.

[0078] **Fig. 6** is a drawing of a hybrid fluidized bed reactor **600** for forming carbon allotropes. In the hybrid fluidized bed reactor **600** the reactant gases **602** enter the reactor plenum **604** below the distributor plate **606**. The distributor plate **606** distributes the reactant gases **602** into the fluidized bed **608**, maintaining the fluidization of the material in the bed. As the reactant gases **602** pass through the fluidized bed **608**, the reactants are consumed and carbon allotropes, such as carbon nanotubes (CNTs), and water are produced. The carbon allotropes are attrited from the surface of the catalyst and move into the expanded bed area **610**. Lighter catalyst particles, with active catalyst sites, are also carried into the expanded bed area **610**, where their residence time is increased and further reaction takes place. The increased area of the expanded bed area **610** decreases the velocity of the reactant gases **602**, allowing heavier catalyst particles to settle back into the fluidized bed **608**.

[0079] The carbon allotropes are eventually eluted from the expanded bed area **610** in an effluent stream **612** that includes product gases, catalyst particles, and the carbon allotropes. The effluent stream is passed to a catalyst separation cyclone **614**. In the catalyst separation cyclone **614**, the product gases **616**, including the carbon allotropes, are separated from the eluted catalyst particles **618**. The catalyst particles **618** are returned to the fluidized bed **608**. The product gases **616** and the carbon allotropes are passed to a product separation cyclone **620**, where the carbon allotropes **622** are removed from the product gases **616**. The resulting recycle gases **624** may then be recycled in the process, for example, as waste gas stream **326 (Fig. 3) or 426 (Fig. 4)**.

[0080] Fresh catalyst **626** is fed from a catalyst feed vessel **628** to the fluidized bed **608** using a lock hopper system that includes two valves **630** and **632** and a lock hopper **634**. The lock hopper **634** is pressurized with reactant gases **602**, to eliminate air before the catalyst **626** is fed to the reactor plenum **604**.

[0081] A spent catalyst removal system may be used to continuously remove spent catalyst **636** and other solid wastes from the reactor. The spent catalyst removal system can include a pipe **638** that projects through the distributor plate **606** and leads to a valve **640**, a lock hopper **642**, and another valve **644**. The valves **640** and **644** allow material that is removed from the reactor **600** to be cooled, depressurized, and purged with an inert gas prior to be dropped into a spent catalyst vessel **646**.

[0082] The design of the reactor **600** can control the various time scales for reaction, attrition, and carbon allotrope growth in both the lower fluid bed **608** and the expanded bed area **610**. For example, the residence times can be controlled with the diameter and height of the fluidized bed **608**, the degree of expansion from the fluidized bed **608** to the expanded bed area **610**, and the height of the expanded bed area **610**. The rate of attrition, i.e., the separation of carbon allotropes from catalyst particles, can be controlled by the amount of fluidization in the fluidized bed **608**, for example, by increasing or decreasing the flow rate of the reactant gases **602**. The rate of loss of the catalyst can be controlled by the rate of withdrawal of spent catalyst **635**, and subsequent feed of fresh catalyst **626** to maintain a steady state. This can also be balanced by the rate of reaction to produce carbon allotropes, and the inherent loss of catalyst that is carried out of the hybrid fluidized bed reactor **600** with the carbon allotropes **622** that are produced.

[0083] A number of modifications may be made to the reactor design discussed with respect to **Fig. 6** to change the time scale of the phenomena. As discussed with respect to the following figures, a reactor may be recirculated, have a packed bed, a bottom feed, or any combinations thereof. Further, multiple reactor concepts may be combined to capitalize on the different time scales for different phenomena in each design.

[0084] **Fig. 7** is a drawing of another hybrid fluidized bed reactor **700** for forming carbon allotropes. Like numbered items are as described with respect to **Fig. 6**. This reactor **700** includes a fluidized bed **702** and a transport reactor **704** operated in parallel. The reactant feed **706** is split, with a first portion **708** of the reactant feed **706** going into a jet that feeds the fluidized bed **702** and the balance **710** of the reactant feed **706** going to the transport reactor **704**. As a result of this design, the catalyst circulates from the fluidized bed **702** to the transport reactor **704**. The gas discharge **712** from the transport reactor **704** to the fluidized bed **702** may be arranged to aid in the separation of the catalyst particles from the gas stream **714** so that the particles fall to the fluidized bed **702** as the effluent stream **612** exits to the catalyst separation cyclone **614**.

[0085] The growth time in the transport reactor **704** can be controlled by the gas flow rate so that it is slightly larger than the terminal settling velocity of the catalyst grit. The terminal settling velocity of a particle is the falling velocity of the particle in a quiescent fluid once the velocity has reached steady state. It is also affected by the concentration of particles in the fluid, with higher particle concentrations resulting in lower terminal settling velocities. The growth time in the fluidized bed **702** is controlled by the diameter and height of the fluidized bed **702**. The carbon allotrope attrition rate is controlled the fluidization regime in the bubbling fluidized bed **702**. As in the reactor **600** discussed with respect to **Fig. 6**, there is a lock hopper **634** for the addition of fresh catalyst and two cyclonic separators, a catalyst separation cyclone **614** and a product separation cyclone **620**. As shown, the catalyst particles **618** captured in the catalyst separation cyclone **614** are diverted to a spent catalyst vessel **642** for disposal. However, the catalyst particles **618** may be returned from the catalyst separation cyclone **614** to either the fluidized bed **702** or the transport reactor **704**. Also, additional carbon allotrope product may be captured from the gas discharge of the product separation cyclone **620**, by using a high efficiency particulate capture system, such as multiclones or a particulate filter, among others.

[0086] An advantage of the design of the reactor **700** shown in **Fig. 7** is the control over the growth time for carbon allotropes. The transport reactor **704** can be operated in a plug-flow manner, in which all of the particles have the same residence time, allowing the growth time to be closely controlled. Further, there is good gas-solid contact in the transport reactor **704**. The lack of a distributor plate in the transport reactor **704** also decreases the likelihood of plugging. The transport reactor **704** may also be constructed substantially entirely of refractory lined steel to minimize or eliminate metallic components in direct contact with the potentially corrosive process gas.

[0087] **Fig. 8** is a drawing of a hybrid packed bed reactor **800** for forming carbon allotropes. Like numbered items are as described with respect to **Fig. 6**. This reactor **800**, which is a variant of the design for the reactor **600** shown in **Fig. 6**, uses a packed bed **802** rather than the fluidized bed **608** discuss with respect to **Fig. 6**. The packed bed reactor **802** may be used with occasional periods of significantly higher flows of reactant gas **804**, e.g., pulses, during which the packed bed **802** becomes fluidized. During the pulses, carbon allotropes are attrited from the catalyst surface. An expanded bed area **610** allows material to slow and settle back to the packed bed **802**. Effluent gases **612** are passed to a catalyst separation cyclone **614**, which can remove the catalyst particles **618** and return them to the packed bed **802**. Depending on the ratio of the diameter of the expanded bed area **610** to the packed bed **606**, the catalyst separation cyclone **614** may be eliminated. Carbon allotropes **622**, such as CNTs, are removed by a product separation cyclone **620**, primarily during the pulses, although some carbon allotropes **618** may carried out of the reactor **800** during the period of time between pulses.

[0088] In reactor **800**, the growth time for the carbon allotropes **622** is uniquely controlled by the time the reactor **800** is operated in normal (unpulsed) packed bed operation. The attrition time is uniquely controlled by the pulse time when the packed bed **802** becomes fluidized during the pulses. Accordingly, the time between pulses may be used to control production efficiency, product properties, or both.

[0089] **Fig. 9** is a drawing of a hybrid spouted bed reactor **900** for forming carbon allotropes. Like numbered items are as described with respect to **Fig. 6**. This reactor **900** is also a variant of the reactor **600** discussed with respect to **Fig. 6**. In the reactor **900**, a spouted bed **902** is used instead of a fluidized bed. A disengaging section **904** allows particles to slow and fall back into the spouted bed **902**. This reactor **900** can utilize somewhat larger catalyst particles than a typical fluidized bed and does not require the use of a gas distribution grid.

[0090] As the catalyst particles degrade, forming smaller particles, they can be carried up into a swage **906** that opens up into an expanded bed area **908**. Depending on the width of the expanded bed area **908**, the amount of catalyst particles carried out in the reactor effluent **612** may be very low. Accordingly, two product separation cyclones **620** may be used instead of a catalyst separation cyclone, enhancing the amount of product isolated. However, in some circumstances, it may be desirable to use a catalyst separation cyclone in place of the first product separation cyclone **620**, and direct the isolated material back to the reactor **900**.

[0091] **Fig. 10** is a drawing of hybrid packed/fluidized bed reactor **1000** for forming carbon allotropes. Like numbered items are as described with respect to **Fig. 6**. In this reactor **1000**, the reactant gases **602** enter through a line **1002** at the bottom of the reactor **1000**. Fresh catalyst particles **626** are introduced in the reactant gases **602**, and the mixture **1004** is transported by the high velocity flow of the reactant gases **602**. Reaction particles **1006** are dropped into the mixture **1004** through a control valve **1008** at the bottom of the reactor **1000**. The resulting gas/particulate mixture **1010** proceeds through the line **1002** at high velocity, transporting the mixture **1010** to the upper part of the reactor **1000**, where the particles drop onto a moving packed bed **1012**. The moving packed bed **1012** drops downward in the annular part **1014** of the body of the reactor **1000**. The reactant gases **602** also move downward in the annular part **1014** of the body of the reactor **1000**, turn and go upward in a pipe section **1016** internal to the body of the reactor **1000**. Reactor effluent **612**, carrying product and catalyst exits the reactor **1000** through the pipe section **1016** at the top of the reactor **1000**. In the pipe section **1016**, a fluidized bed **1018** is formed.

[0092] In the reactor **1000**, the growth time for carbon allotropes is controlled primarily by the depth and cross sectional area of the packed bed **1012**. The ratio of gas flow leaving the reactor to that being recycled in the reactor may also influence the growth time. Freeboard carbon allotrope growth is not needed in this reactor design. The residence time of the catalyst is controlled by the flow rate of catalyst into the reactants at the bottom of the reactor. The time for attrition is controlled by the height and diameter of the fluidized bed **1018**. The feed points for fresh catalyst **626** and for reaction particles **1006** that are being recirculated can be of designs typically used for the feed systems for sand blasting. In the reactor **1000**, the carbon allotrope growth time can be controlled separately from the catalyst residence time. Further, the attrition time can be controlled separately by the residence time in the fluidized bed **1018**.

[0093] Other arrangements of this concept are possible, for example side-by-side reactors in which solids are withdrawn from each reactor with standpipes and returned to each with gas-solid transport lines. Another alternative is to have the fluidized bed reactor above the fixed bed reactor. A further alternative would be to arrange the gas and solids to be countercurrent with solids flow downwards and gas flow upwards.

[0094] **Fig. 11** is a drawing of a two hybrid reactor system **1100** for forming carbon allotropes. Like numbered items are as described with respect to **Fig. 6**. This reactor system **1100** is a variant of a hybrid fixed bed and fluidized bed reactor system, for example, as discussed with respect to **Fig. 10**. In contrast to reactor **1000**, the fixed bed reactor **1102** and the fluidized bed reactor **1104** are separate vessels that are optimized for each reactor type. The primary carbon allotrope growth reaction occurs in the fixed bed reactor **1102**, while the fluidized bed reactor **1104** is used to separate the product carbon allotrope from the catalyst particles by attrition.

[0095] In this example, the fixed bed reactor **1102** is disposed above the fluidized bed reactor **1104**. Catalyst particles **1106** are transported to the inlet **1108** of the fixed bed reactor **1102** in a mixture **1110** with preheated feed gas **602**. The mixture

1110 travels down the fixed bed reactor **1102** to a separation zone **1112** where gas **1114** is separated from the reacted particles **1116**. The gas **1114** is recycled in the process, for example, in combination with waste gas stream **326 (Fig. 3)** or **426 (Fig. 4)**. The reacted particles **1116** are sent to the fluidized bed reactor **1104**.

[0096] In the fluidized bed reactor **1104**, the reacted particles **1116** are fluidized with a portion of the feed gas **602**. The primary function of the fluidized bed reactor **1104** is to separate the carbon allotrope product from catalyst particles by attrition, although, depending on conditions, some reaction may be occurring here as well. Attrition aids, such as gas jet attriters may be included in the fluidized bed reactor **1104** to enhance the separation of the carbon allotrope product from the catalyst particles. The separated carbon allotrope product is carried with the gas to gas/solid separation systems, such as product separation cyclones **620**, to recover the carbon allotrope product. Catalyst particles **1106** are withdrawn from the fluidized bed reactor **1104**, for example, by a standpipe **1120**, and may then be returned to the fixed bed reactor **1102** in a gas-solid transport line **1122** in the mixture **1110** with the preheated feed gas **602**. In one embodiment, a portion of the catalyst particles **1106** are disposed of as spent catalyst.

[0097] Reactions forming carbon allotropes

[0098] **Fig. 12** is a schematic of a catalytic reaction **1200** for the formation of carbon allotropes, such as carbon nanotubes (CNTs), on a catalyst bead **1202**. An initial reaction **1204** between a portion of the CH_4 and the CO_2 in the hot gas feed stream **1206** results in the formation of CO and H_2 in stoichiometric amounts. Excess amounts of the source gases **1206** continue to flow through the reactor, helping to fluidize the bed (if needed), and carrying away CNTs **1208** and catalyst particles **1210**.

[0099] The reactions that form the CNTs **1208** take place on the catalyst bead **1202**. The size of the CNTs **1208**, and the type of CNTs **1208**, e.g., single wall or multiwall CNTs **1208**, may be controlled by the size of the grains **1212**. 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 **1202**.

Generally, smaller grains **1212** will result in fewer layers in the CNTs **1208**, and may be used to obtain single wall CNTs **1208**. Other parameters may be used to affect the morphology of the final product as well, including reaction temperature, pressure, and feed gas flow rates.

[0100] The CO and H_2 react at grain boundaries **1214**, lifting active catalyst particles **1216** off the catalyst bead **1202**, and forming H_2O **1218** and the solid carbon of the CNTs **1208**. The CNTs **1208** break off from the catalyst bead **1202** and from the catalyst particle **1210**. Larger catalyst particles **1210** can be captured and returned to the reactor, for example, by the catalyst separator **518** discussed with respect to **Fig. 5**, or by catalyst separation zones in the reactor designs discussed with respect to **Figs. 6 – 11**. Very fine catalyst particles **1210** will be carried out with the CNTs **1208**. The final product will include about 95 mol % solid carbon and the balance from the catalyst materials, including, for example, iron. The CNTs **1208** will often agglomerate to form clusters **1220**, which are the common form of the final product. Some amount of the CO and H_2 passes through the reactor without reacting and are contaminants in the reactor effluent streams.

[0101] As the reaction proceeds, the catalyst bead **1202** is degraded and finally consumed. Accordingly, the catalytic reaction **1200** 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.

[0102] The catalyst bead **1202** can include any number of other metals, such as nickel, ruthenium, cobalt, molybedenum, and others, including non-reactive metals such as copper, tin, or aluminum, among others. However, the catalytic sites on the catalyst beads **1202** are principally composed of iron atoms. In one embodiment, the catalyst bead **1202** includes metal shot, for example, about 120-25 mesh (0.125 mm to 0.710 mm) metal beads that are used for shot blasting. In one embodiment, the catalyst may be a stainless ball bearing, and the like.

[0103] Gas Separation System

[0104] **Fig. 13** is a simplified process flow diagram of a gas separation system **1300** that can be used in a reactor system for the production of carbon allotropes. The gas separation system **1300** is a bulk fractionation process that may be used with a high CO_2 reactor system, such as that discussed with respect to **Fig. 4**. However, other technologies may be used in embodiments described herein, such as gas adsorption/desorption separation systems.

[0105] In the gas separation system **1300**, the feed gas **1302** is fed to a dryer **1304** to reduce the dew point to about -40 ºC (about -40 ºF), about -50 ºC (about -58 ºF), about -56.7 ºC (about -70 ºF), about -60 ºC (about -76 ºF), about -70 ºC (about -94 ºF), about -80 ºC (about -112 ºF), or lower. The feed gas **1302** can correspond to the dried gas stream **366** discussed with respect to **Figs. 3** and **4**. The dryer **1304** 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. Referring also to Fig. 3, in some embodiments, the dryer can be located prior to the compressor **338**, which may eliminate the need for the ambient temperature heat exchanger **332**.

[0106] The dry gas feed **1306** is then fed through a cryogenic chiller **1308** to reduce the temperature in preparation for the separation. As CO_2 will condense from the gas at about -61 ºC (about -77 ºF), a multistage chilling system **1310** may be used to reduce the temperature to around this level. The multistage chilling system **1310** may include a heat recovery system **1312** used to heat the outlet gas with energy **1313** from the dry feed gas **1306**.

[0107] The chilled feed **1316** is fed to a separation vessel **1318** to separate a liquid stream **1320** and a vapor stream **1322**. The vapor stream **1322** is passed through an expander **1324** to lower the temperature by generating mechanical work **1326** in an adiabatic expansion process. In one embodiment, the mechanical work **1326** is used to drive a generator **1328**, which may provide a portion of the electricity used in the plant. In another embodiment, the mechanical work **1326** is used to drive a compressor, for example, for compressing a refrigerant stream for the multistage chilling system **1310**. The expansion can result in a two phase stream **1330**.

[0108] The liquid stream **1320** and the two phase stream **1330** are fed to a separation column **1332**, for example, at different points along the separation column **1332**. Heat is supplied to the separation column **1332** by a reboiler **1334**. The reboiler **1332** is heated by a stream from a heat exchanger **1336**. The heat exchanger **1336** may be part of a chiller system that is warmer than the separation column **1332**, although below ambient temperature. The column bottom stream **1338** is passed through the reboiler **1334** and a portion **1340** is reinjected after being warmed. An outlet stream **1342** from the reboiler **1334** provides the CO_2 product **1344**. A portion **1346** of the CO_2 product **1344** may be recycled through the heat exchanger **1336** to carry energy to the reboiler **1334**.

[0109] The overhead stream **1348** from the separation column **1332** is a methane enhanced stream, for example, including about 55 mol % CH_4 and about 40 mol % CO_2, about 60 mol % CH_4 and about 35 mol % CO_2, about 70 mol % CH_4 and about 25 mol % CO_2, about 73 mol % CH_4 and about 23 mol % CO_2, or about 80 mol % CH_4 and about 15 mol % CO_2. As noted, the overhead stream **1348** may be used in a chiller system **1312** to cool the dry gas feed **1306**, warming the overhead stream **1348** to form the recycle gas **1350**. Other components may be present in the recycle gas **1350** including, for example, about 1 mol % CO and H_2, about 2 mol % CO and H_2, about 3.5 mol % CO and H_2, about 4 mol % CO and H_2, or about 5 mol % CO and H_2.

[0110] The configurations and units discussed with respect to **Figs. 13** 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.

[0111] Packaging System

[0112] **Fig. 14** is a simplified process flow diagram of a packaging system **1400** that can package carbon allotropes **324** separated from an effluent stream from a reactor system. The packaging system **1400** overlaps the lock hopper **422** of the separation system **418** shown in **Fig. 4**, and is used to isolate the carbon allotropes from the process for packaging.

[0113] The packaging system **1400** is part of a packaging train **1402**. The packaging train **1402** may have a sampling valve **1404** to remove carbon allotropes from the lock hopper **422**. The sampling valve **1404** may be a rotary valve configured to allow a certain amount of carbon allotropes and gas through during a portion of a rotation cycle. In some embodiments, the sampling valve **1404** may be a ball valve or gate valve configured to open fully for a selected period of time to allow a selected amount of carbon allotropes and gas through, prior to closing fully. The carbon allotropes and gas are allowed to flow into a drum **1406** for purging and cooling.

[0114] After the sampling valve **1404** has closed, a purge stream **1408** may be opened into the drum **1406** to sweep out remaining gases, such as CO, H_2, H_2O, and CH_4. As noted, the purge stream **1408** may be taken from the CO_2 enriched side of the gas separation system, for example, as purge gas stream **430**, discussed with respect to **Fig. 4**. The purge outlet stream **1410** will carry some amount of carbon allotropes, and other fine particles, and may be passed through a filter **1412**, prior to being sent back to the process as a purge return **1414**. The filter **1412** may be a bag filter, cyclonic separator, or any other suitable separation system. After purging is completed, a packaging valve **1416** will open to allow a stream **1418** including carbon allotropes to flow to a filling station **1420** to be packaged in drums or tanks for sale.

[0115] The isolation system described above is merely exemplary. Any number of other systems may be used in embodiments. However, the carbon allotropes, such as CNTs, may 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.

[0116] Method

[0117] **Fig. 15** is a method **1500** for generating carbon allotropes, such as CNTs, from a feed gas that includes methane and carbon dioxide. Although the method is described for CNTs, it can be understood to apply to other carbon allotropes. The method **1500** begins at block **1502**, at which a mixed CO_2 / CH_4 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, or industrial operations. Further, other feedstocks may be used in embodiments, including other materials, such as syngas, CO, H_2, other hydrocarbons, and the like.

[0118] At block **1504**, 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 cryogenic gas fractionation, as well as any number of other techniques. At block **1506**, the combined gas stream is heated with waste heat recovered from the reaction process. After heating, at block **1508**, the combined gas stream is reacted with a metal catalyst in a hybrid reactor to form the CNTs. At block **1510**, the CNTs are separated from the waste gas. At block **1512**, the separated CNTs are purged, cooled, and packaged to be sent to market.

[0119] 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 **1506**-**1514** will be repeated for each sequential reactor in the reaction system.

[0120] At block **1516**, the waste gas is separated into a CO_2 enriched stream and a CH_4 enriched stream. At block **1518**, whichever stream contains the excess reagent can be sold, while the other stream can be recycled to block **1504** to be used in the process.

[0121] Still other embodiments of the claimed subject matter may include any combinations of the elements listed in the following numbered paragraphs:

1. A reactor system for the production of carbon allotropes, including a hybrid reactor configured to form carbon allotropes from a reactant gas mixture in a Bosch reaction, wherein the hybrid reactor includes at least two distinct zones that

perform different functions including reaction, attrition, catalyst separation, or gas separation.

2. The system of paragraph 1, wherein the hybrid reactor includes:

a first zone including a fluidized bed disposed in a narrow portion of a reactor vessel; and

a second zone including an expanded area bed disposed in a wider portion of the reactor vessel, wherein a reactant gas stream in the reactor flows from the narrow fluidized bed to the wider fluidized bed.

3. The system of paragraph 2, wherein the expanded area bed is configured to slow the reactant gas stream to allow catalyst particles to fall back into the fluidized bed.

4. The system of any of paragraphs 1, 2, or 3, wherein the hybrid reactor includes:

a first zone including a fluidized bed reactor; and

a second zone including a transport reactor, wherein the transport reactor is configured to circulated a portion of the material from the fluidized bed reactor to an opposite end of the fluidized bed reactor.

5. The system of paragraph 4, including dividing a reactant gas stream into portions, wherein a first portion of the reactant gas stream is injected into the fluidized bed to maintain fluidization, and a second portion of the reactant gas stream is injected into the transport reactor to push material through the transport reactor.

6. The system of any of the proceeding paragraphs, wherein the hybrid reactor includes:

a first zone including a packed bed; and

a second zone including an expanded bed area, wherein a reactant gas stream flows through the packed bed before flowing through the expanded bed area.

7. The system of paragraph 6, wherein the reactant gas stream is intermittently pulsed to fluidize the packed bed.

8. The system of paragraphs 6 or 7, wherein the expanded area bed is configured to slow the reactant gas stream to allow catalyst particles to fall back into the packed bed.

9. The system of any of the proceeding paragraphs, wherein the hybrid reactor includes:

a first zone including a spouted bed;

a second zone including a disengaging section configured to allow catalyst particles to drop back to the spouted bed; and

a third zone including an expanded bed area, wherein the expanded bed area is configured to slow a reactant gas flow and allow smaller particles to fall back to the spouted bed.

10. The system of any of the proceeding paragraphs, wherein the hybrid reactor includes:

a first zone including a packed bed disposed in an outer annulus of the hybrid reactor; and

a second zone including a fluidized bed disposed in an inner annulus of the hybrid reactor.

11. The system of paragraph 10, wherein a reactant gas flows through the packed bed and then into the fluidized bed.

12. The system of either of paragraphs 10 or 11, wherein a material in the packed bed flows out of the bottom of the hybrid reactor into a high velocity stream of reactant gas, and wherein the high velocity stream of reactant gas recirculates the material to the top of the hybrid reactor.

13. The system of either of paragraphs 10, 11, or 12, wherein fresh catalyst is fed into the high velocity stream of reactant gas.

14. The system of any of the proceeding paragraphs, wherein the hybrid reactor includes:

a first reactor including:

a first zone including a packed bed; and a second zone including a separation zone, wherein the separation zone is configured to remove a gas from the packed bed; and

a second reactor including a third zone including a fluidized bed, wherein material from the packed bed of the first reactor flows into the fluidized bed of the second reactor.

15. The system of paragraph 14, wherein the fluidized bed attrits carbon allotropes from the material.

16. The system of any of the proceeding paragraphs, including a catalyst separation cyclone configured to remove catalyst particles from an effluent stream from the hybrid reactor and return the catalyst particles to the hybrid reactor.

17. The system of any of the proceeding paragraphs, including a fresh catalyst feed system configured to provide fresh catalyst to a reaction zone in the hybrid reactor.

18. The system of any of the proceeding paragraphs, including a spent catalyst removal system configured to remove material from a reaction zone.

19. The system of any of the proceeding paragraphs, including a product separation cyclone configured to remove a carbon allotrope from an effluent stream.

20. The system of any of the proceeding paragraphs, including at least two product separation cyclones in a series configuration, wherein each product separation cyclone configured to remove a carbon allotrope from an effluent stream.

21. A method for forming carbon allotropes, including:

injecting a reactant gas into a hybrid reactor, wherein the hybrid reactor includes at least two zones, and wherein each zone performs a function including reaction, catalyst separation, attrition, or gas separation, and wherein the reactant gas includes a carbon oxide and a hydrocarbon;

forming carbon allotropes in the hybrid reactor using a Bosch reaction;

separating catalyst particles from the reactant gas to form a waste gas stream; and

separating the carbon allotropes from the waste gas stream.

22. The method of paragraph 21, including forming the carbon allotropes in a packed bed.

23. The method of either of paragraphs 21 or 22, including attriting carbon allotropes from a catalyst particle in a fluidized bed.

24. The method of any of paragraphs 21, 22, or 23, including separating a catalyst particle from the reactant gas in an expanded bed area.

25. The method of any of paragraphs 21-24, including forming the carbon allotropes in a transport reactor.

26. A reaction system for forming carbon allotropes, including:

a hybrid reactor configured to form carbon allotropes from gas streams using a Bosch reaction, wherein the hybrid reactor includes at least two distinct functional zones, wherein each zone is configured to perform a function including reaction, attrition, catalyst separation, or gas separation;

a separation system downstream of the hybrid reactor, wherein the separation system is configured to remove carbon allotropes from an effluent from the hybrid reactor;

a feed heater downstream of the separation system, wherein the feed heater includes a heat exchanger configured to heat a feed gas stream for the hybrid reactor using waste heat from the effluent from the hybrid reactor;

a heat exchanger downstream of the separation system, wherein the heat exchanger is configured to remove water from the effluent;

a gas separation 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.

27. The reaction system of paragraph 26, wherein a reactor zone includes a fluidized bed, and wherein the fluidized bed attrits carbon allotropes from a catalyst surface.

28. The reaction system of either of paragraphs 26 or 27, wherein a reactor zone includes a packed bed, wherein the packed bed forms carbon allotropes on a catalyst surface.

29. The reaction system of any of paragraphs 26, 27, or 28, wherein a reactor zone includes an expanded bed area, wherein the expanded bed area slows a gas stream allowing entrained particles to settle out of the gas stream.

30. The reaction system of any of paragraphs 26-29, including a separation vessel downstream of the ambient temperature heat exchanger, wherein the separation vessel is configured to separate liquid water from a gas stream.

[0122] 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 reactor system for the production of carbon allotropes, comprising a hybrid reactor configured to form carbon allotropes from a reactant gas mixture in a Bosch reaction, wherein the hybrid reactor comprises at least two distinct zones that perform different functions comprising reaction, attrition, catalyst separation, or gas separation.

2. The system of claim 1, wherein the hybrid reactor comprises:
   a first zone comprising a fluidized bed disposed in a narrow portion of a reactor vessel; and
   a second zone comprising an expanded area bed disposed in a wider portion of the reactor vessel, wherein a reactant gas stream in the reactor flows from the narrow fluidized bed to the wider fluidized bed.

3. The system of claim 2, wherein the expanded area bed is configured to slow the reactant gas stream to allow catalyst particles to fall back into the fluidized bed.

4. The system of claim 1, wherein the hybrid reactor comprises:
   a first zone comprising a fluidized bed reactor; and
   a second zone comprising a transport reactor, wherein the transport reactor is configured to circulated a portion of the material from the fluidized bed reactor to an opposite end of the fluidized bed reactor.

5. The system of claim 4, comprising dividing a reactant gas stream into portions, wherein a first portion of the reactant gas stream is injected into the fluidized bed to maintain fluidization, and a second portion of the reactant gas stream is injected into the transport reactor to push material through the transport reactor.

6. The system of claim 1, wherein the hybrid reactor comprises:
a first zone comprising a packed bed; and
a second zone comprising an expanded bed area, wherein a reactant gas stream flows through the packed bed before flowing through the expanded bed area.

7. The system of claim 6, wherein the reactant gas stream is intermittently pulsed to fluidize the packed bed.

8. The system of claim 6, wherein the expanded area bed is configured to slow the reactant gas stream to allow catalyst particles to fall back into the packed bed.

9. The system of claim 1, wherein the hybrid reactor comprises:
a first zone comprising a spouted bed;
a second zone comprising a disengaging section configured to allow catalyst particles to drop back to the spouted bed; and
a third zone comprising an expanded bed area, wherein the expanded bed area is configured to slow a reactant gas flow and allow smaller particles to fall back to the spouted bed.

10. The system of claim 1, wherein the hybrid reactor comprises:
a first zone comprising a packed bed disposed in an outer annulus of the hybrid reactor; and
a second zone comprising a fluidized bed disposed in an inner annulus of the hybrid reactor.

11. The system of claim 10, wherein a reactant gas flows through the packed bed and then into the fluidized bed.

12. The system of claim 10, wherein a material in the packed bed flows out of the bottom of the hybrid reactor into a high velocity stream of reactant gas, and wherein the high velocity stream of reactant gas recirculates the material to the top of the hybrid reactor.

13. The system of claim 11, wherein fresh catalyst is fed into the high velocity stream of reactant gas.

14. The system of claim 1, wherein the hybrid reactor comprises:
a first reactor comprising:
a first zone comprising a packed bed; and
a second zone comprising a separation zone, wherein the separation zone is configured to remove a gas from the packed bed; and
a second reactor comprising a third zone comprising a fluidized bed, wherein material from the packed bed of the first reactor flows into the fluidized bed of the second reactor.

15. The system of claim 14, wherein the fluidized bed attrits carbon allotropes from the material.

16. The system of claim 1, comprising a catalyst separation cyclone configured to remove catalyst particles from an effluent stream from the hybrid reactor and return the catalyst particles to the hybrid reactor.

17. The system of claim 1, comprising a fresh catalyst feed system configured to provide fresh catalyst to a reaction zone in the hybrid reactor.

18. The system of claim 1, comprising a spent catalyst removal system configured to remove material from a reaction zone.

19. The system of claim 1, comprising a product separation cyclone configured to remove a carbon allotrope from an effluent stream.

20. The system of claim 1, comprising at least two product separation cyclones in a series configuration, wherein each product separation cyclone configured to remove a carbon allotrope from an effluent stream.

21. A method for forming carbon allotropes, comprising:

injecting a reactant gas into a hybrid reactor, wherein the hybrid reactor comprises at least two zones, and wherein each zone performs a function comprising reaction, catalyst separation, attrition, or gas separation, and wherein the reactant gas comprises a carbon oxide and a hydrocarbon;

forming carbon allotropes in the hybrid reactor using a Bosch reaction;

separating catalyst particles from the reactant gas to form a waste gas stream; and

separating the carbon allotropes from the waste gas stream.

22. The method of claim 21, comprising forming the carbon allotropes in a packed bed.

23. The method of claim 21, comprising attriting carbon allotropes from a catalyst particle in a fluidized bed.

24. The method of claim 21, comprising separating a catalyst particle from the reactant gas in an expanded bed area.

25. The method of claim 21, comprising forming the carbon allotropes in a transport reactor.

26. A reaction system for forming carbon allotropes, comprising:

a hybrid reactor configured to form carbon allotropes from gas streams using a Bosch reaction, wherein the hybrid reactor comprises at least two distinct functional zones, wherein each zone is configured to perform a function comprising reaction, attrition, catalyst separation, or gas separation;

a separation system downstream of the hybrid reactor, wherein the separation system is configured to remove carbon allotropes from an effluent from the hybrid reactor;

a feed heater downstream of the separation system, wherein the feed heater comprises a heat exchanger configured to heat a feed gas stream for the hybrid reactor using waste heat from the effluent from the hybrid reactor;

a heat exchanger downstream of the separation system, wherein the heat exchanger is configured to remove water from the effluent;

a gas separation 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.

27. The reaction system of claim 26, wherein a reactor zone comprises a fluidized bed, and wherein the fluidized bed attrits carbon allotropes from a catalyst surface.

28. The reaction system of claim 26, wherein a reactor zone comprises a packed bed, wherein the packed bed forms carbon allotropes on a catalyst surface.

29. The reaction system of claim 26, wherein a reactor zone comprises an expanded bed area, wherein the expanded bed area slows a gas stream allowing entrained particles to settle out of the gas stream.

30. The reaction system of claim 26, comprising a separation vessel downstream of the ambient temperature heat exchanger, wherein the separation vessel is configured to separate liquid water from a gas stream.

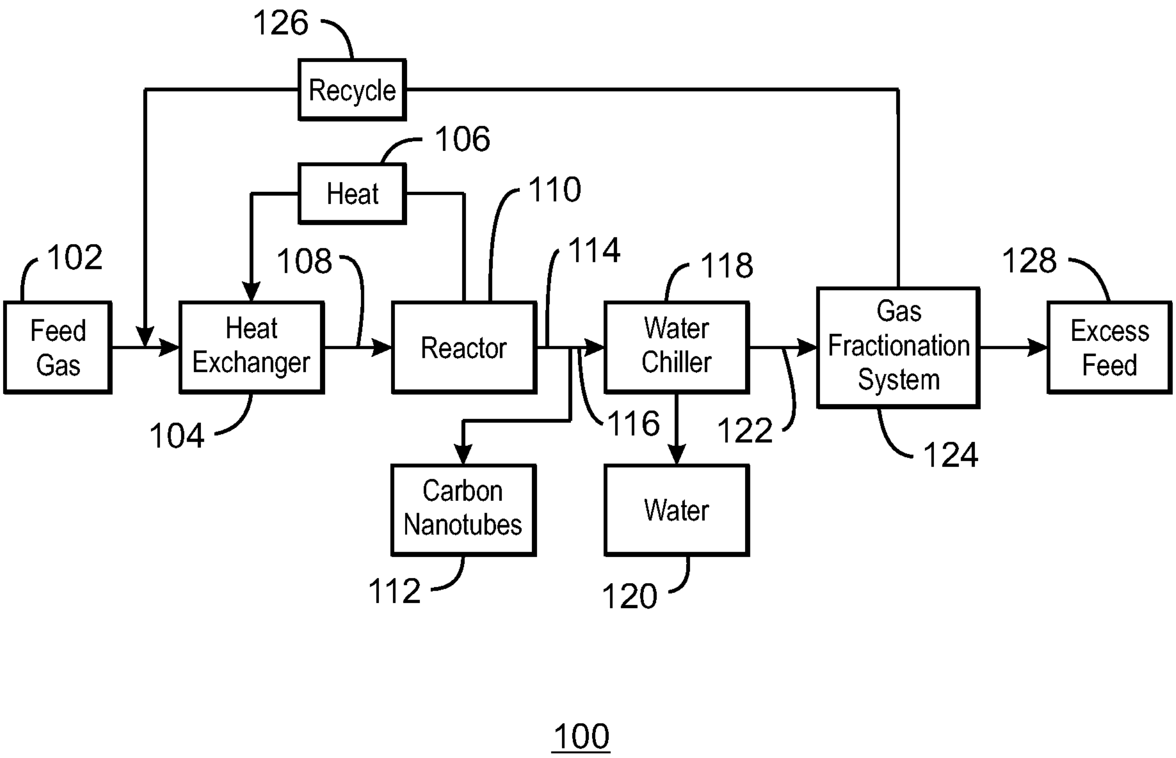


FIG. 1A

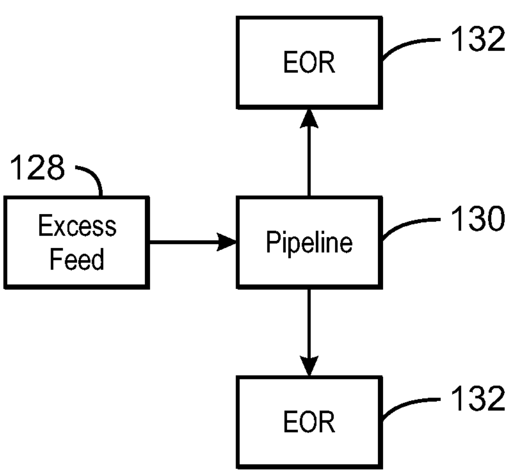


FIG. 1B

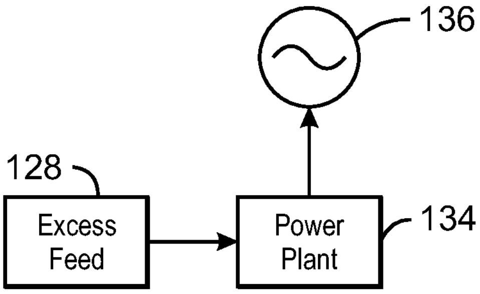
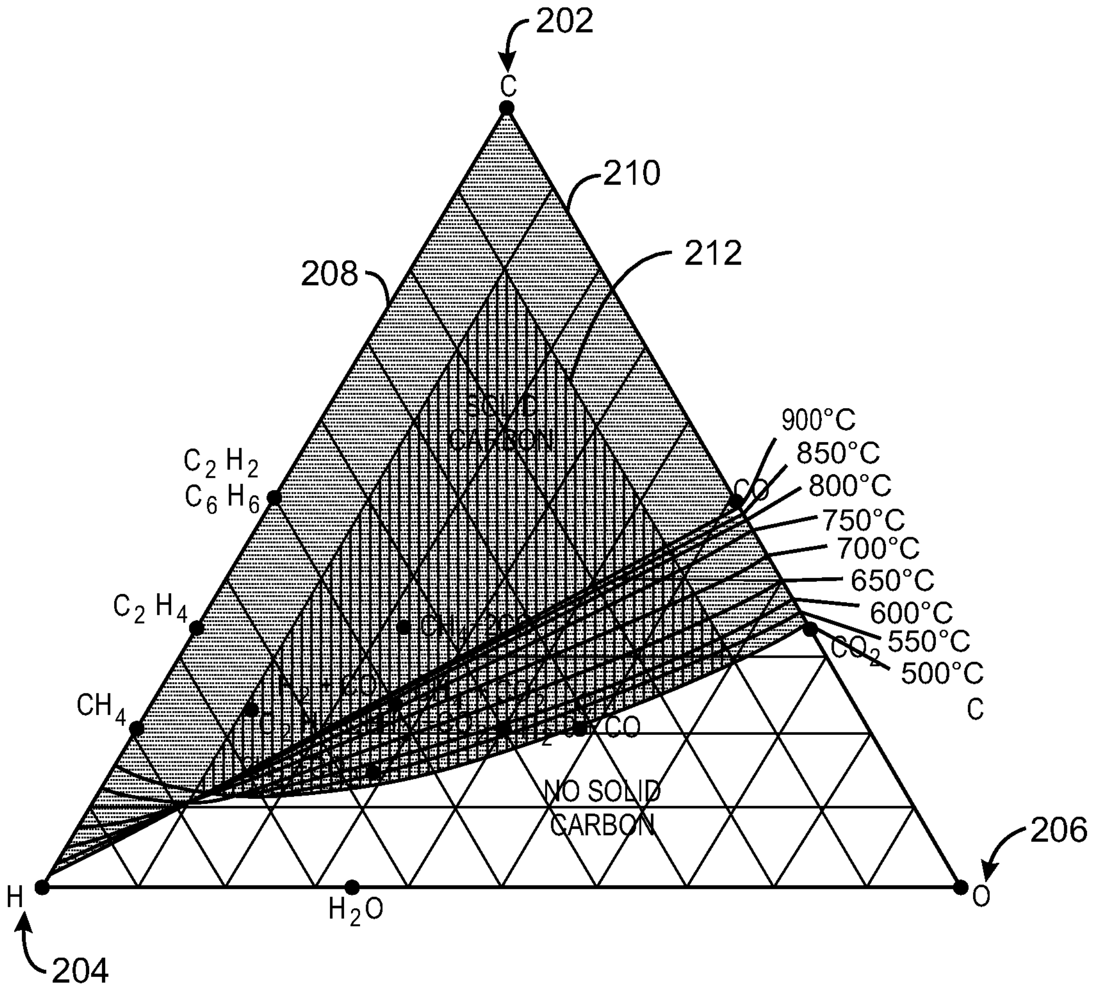


FIG. 1C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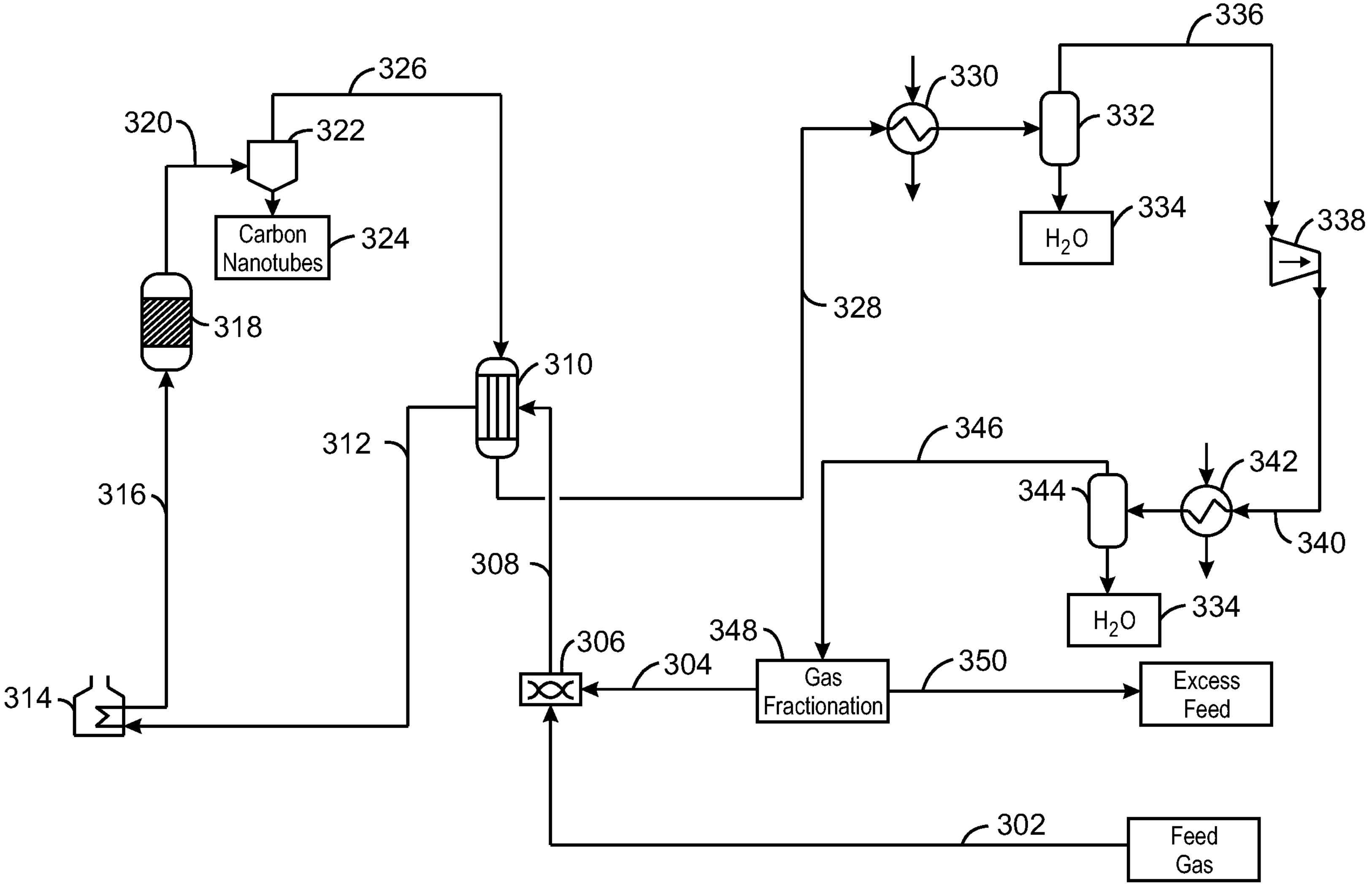
C
210
212
208
SOLID
CARBON
C_2H_2
C_6H_6
C_2H_4
CH_4
$H_2 + CO$
CO
900°C
850°C
800°C
750°C
700°C
650°C
600°C
550°C
500°C
C
CO_2
NO SOLID
CARBON
206
O
H
H_2O
204

200

FIG. 2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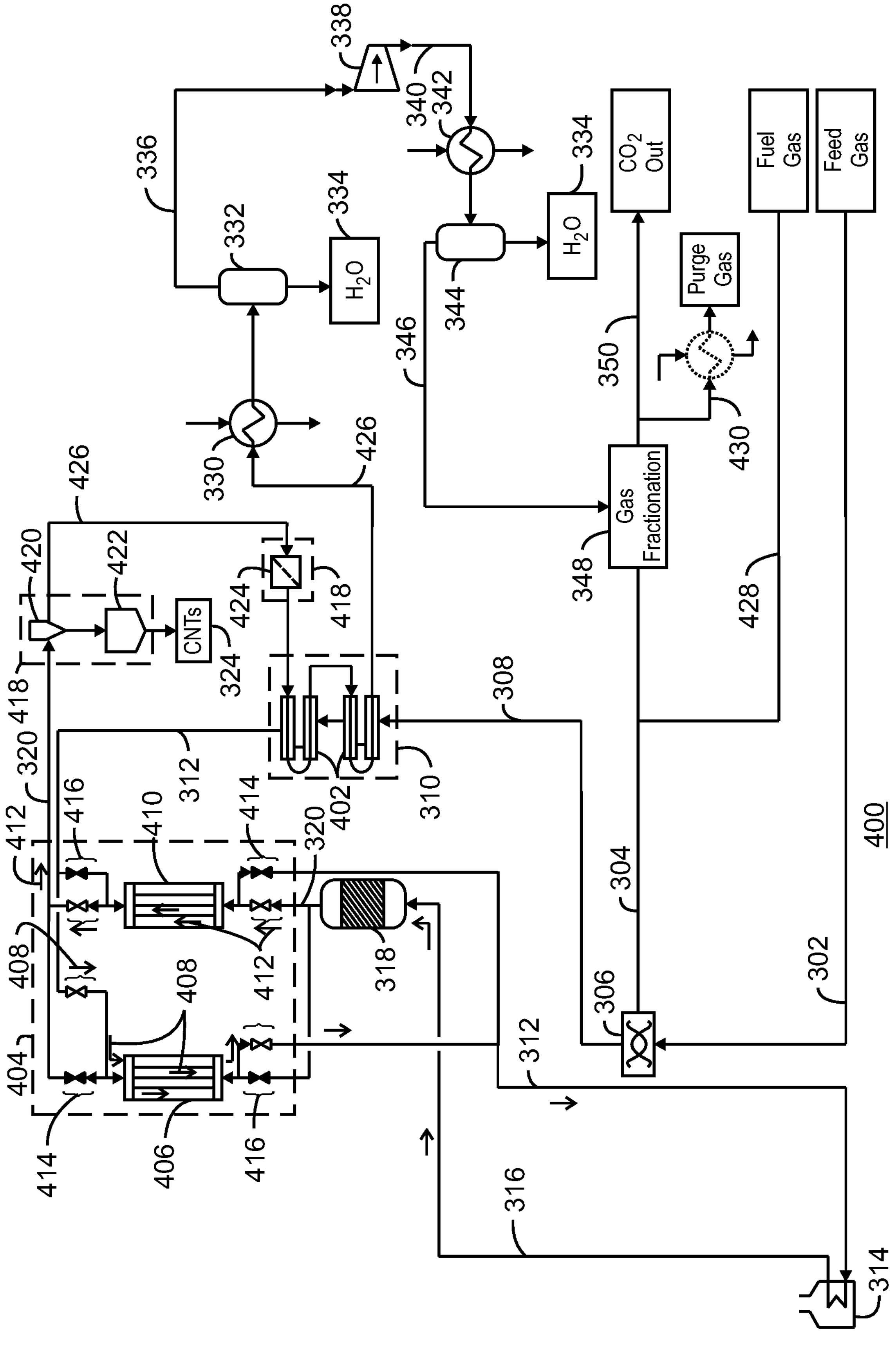
322
326
Carbon Nanotubes
324
318
316
314
312
310
308
306
304
348
Gas Fractionation
350
Excess Feed
302
Feed Gas
328
330
332
336
334
H_2O
338
346
344
342
340
334
H_2O

300

FIG. 3


338
336
340
342
332
334
334
CO2 Out
Fuel Gas
Feed Gas
H2O
H2O
344
346
Purge Gas
350
330
426
426
430
420
422
424
418
348
Gas Fractionation
428
CNTs
324
418
320
308
312
402
310
412
416
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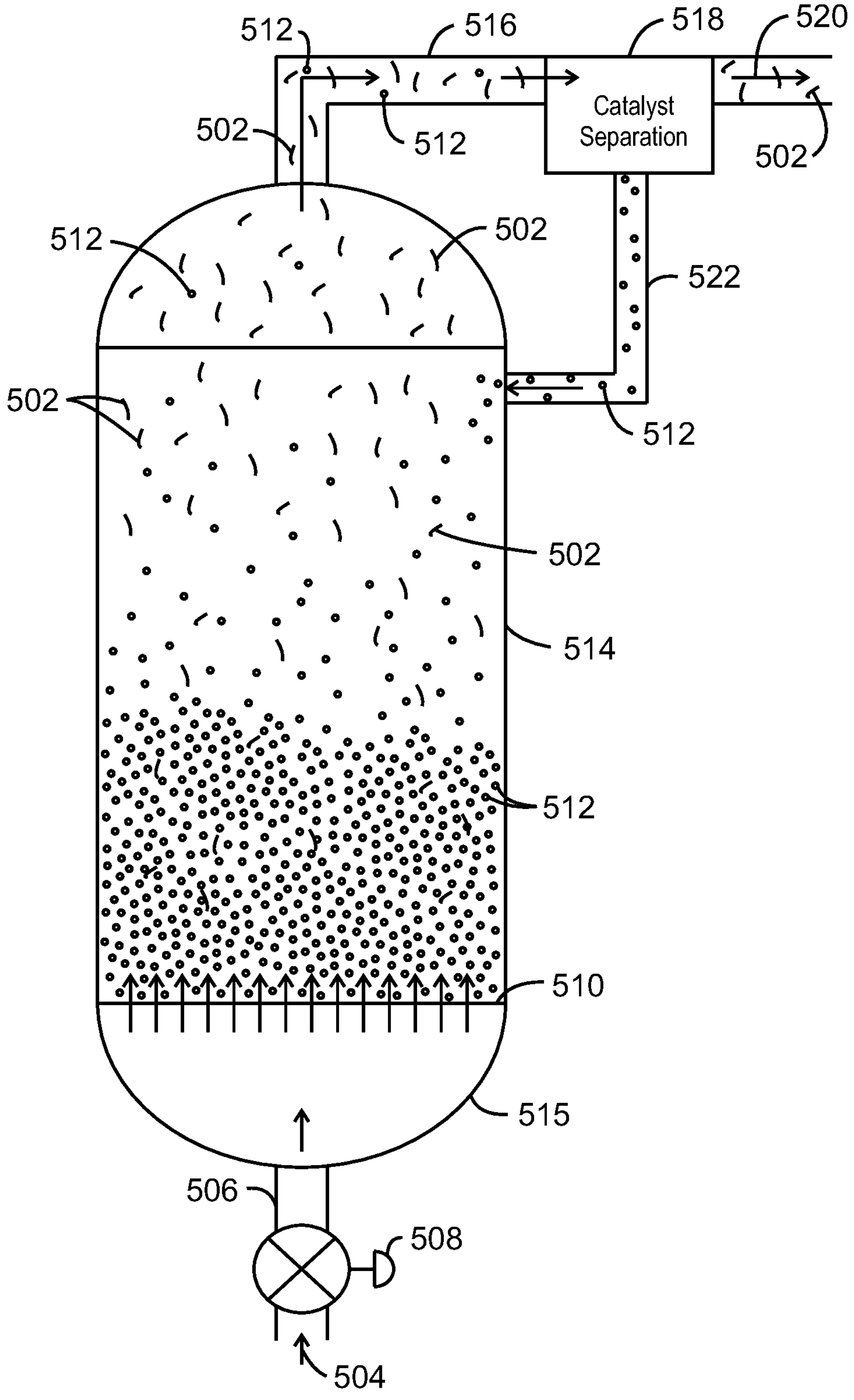
312
302
316
314
400

FIG. 4


512
516
518
520
Catalyst Separation
502
512
502
512
502
522
502
512
502
514
512
510
515
506
508
504

500

FIG. 5

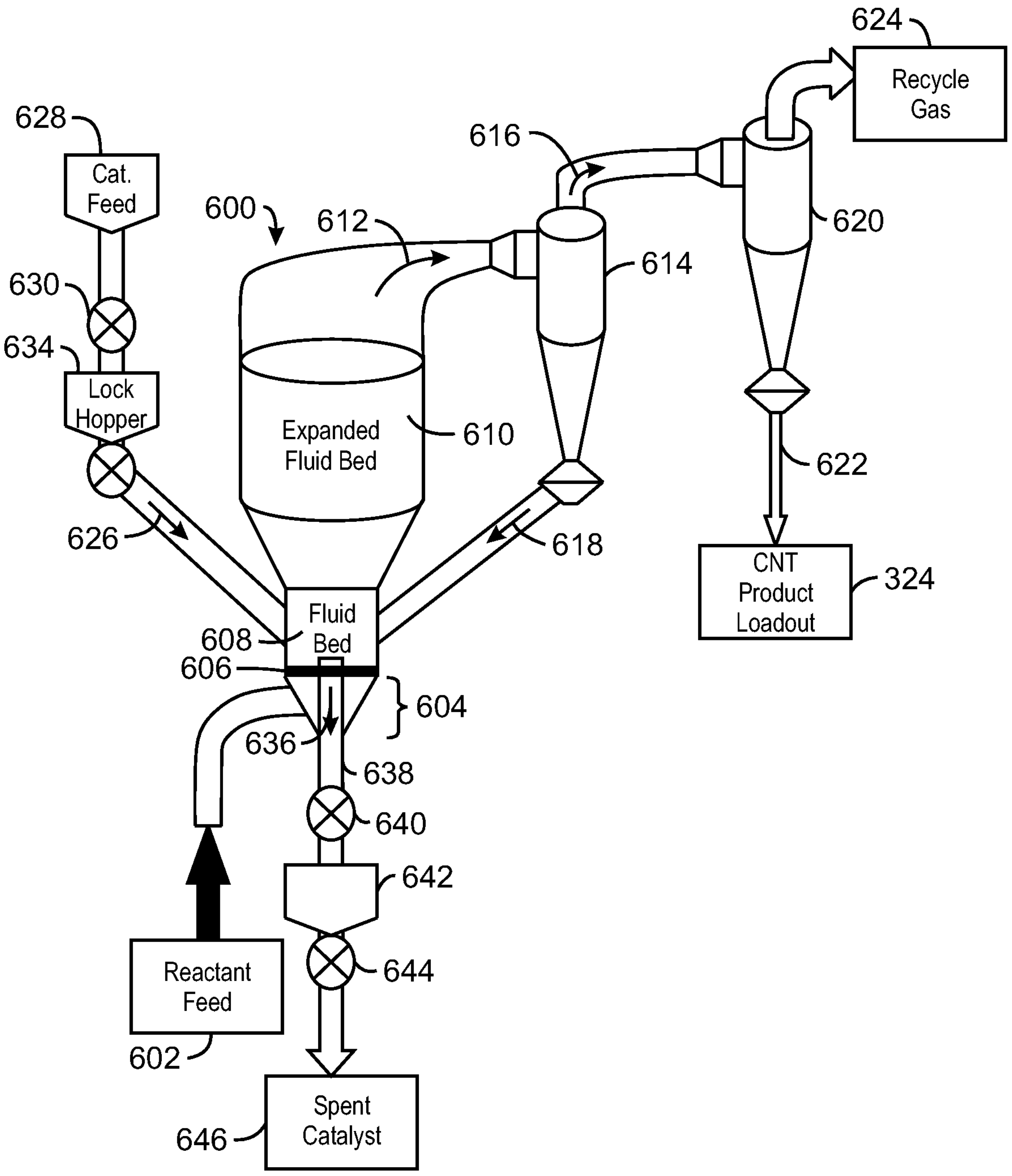

624
Recycle Gas
628
Cat. Feed
616
600
612
620
630
614
634
Lock Hopper
Expanded Fluid Bed
610
622
626
618
CNT Product Loadout
324
Fluid Bed
608
606
604
636
638
640
642
644
Reactant Feed
602
Spent Catalyst
646

FIG. 6

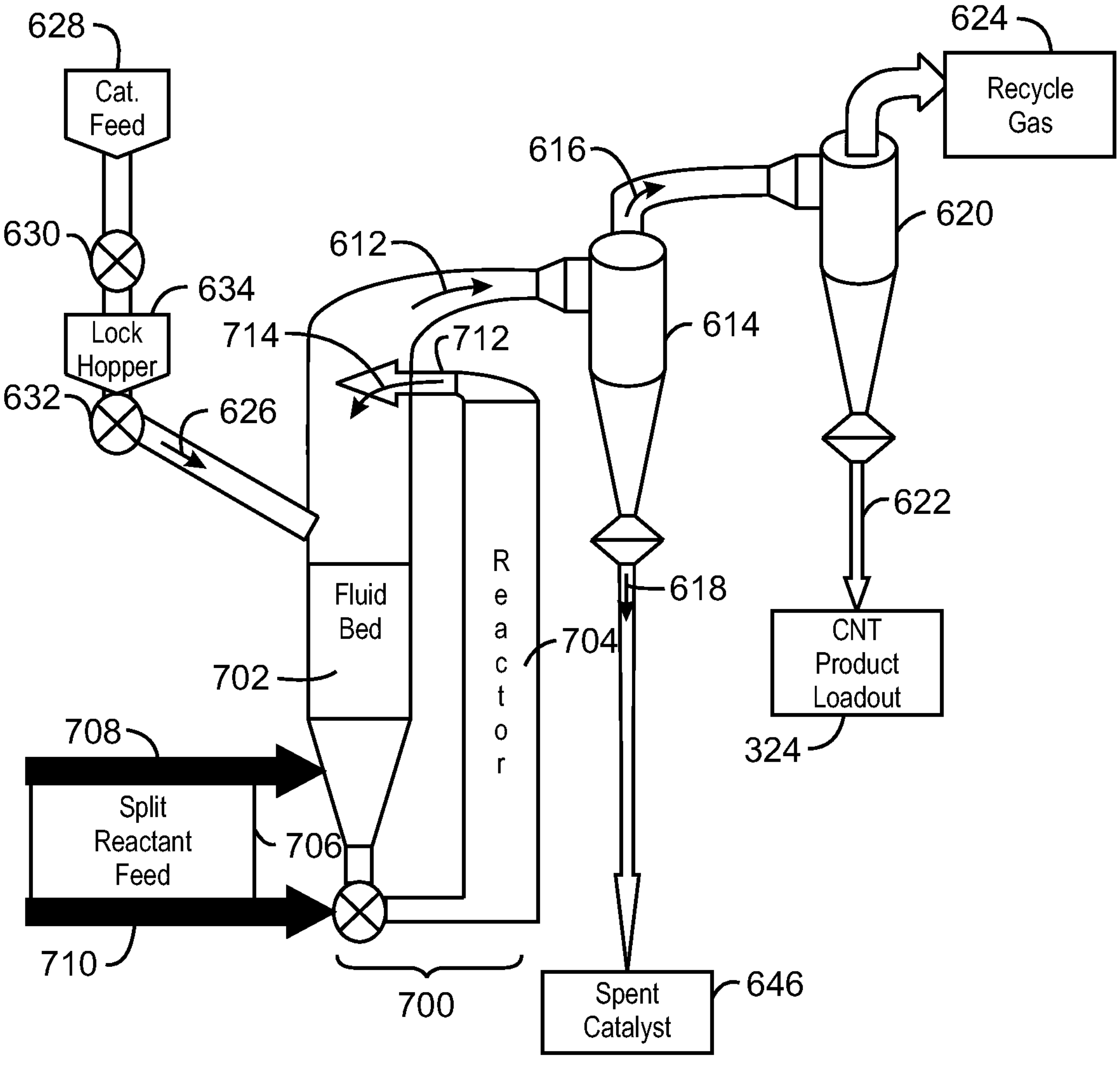
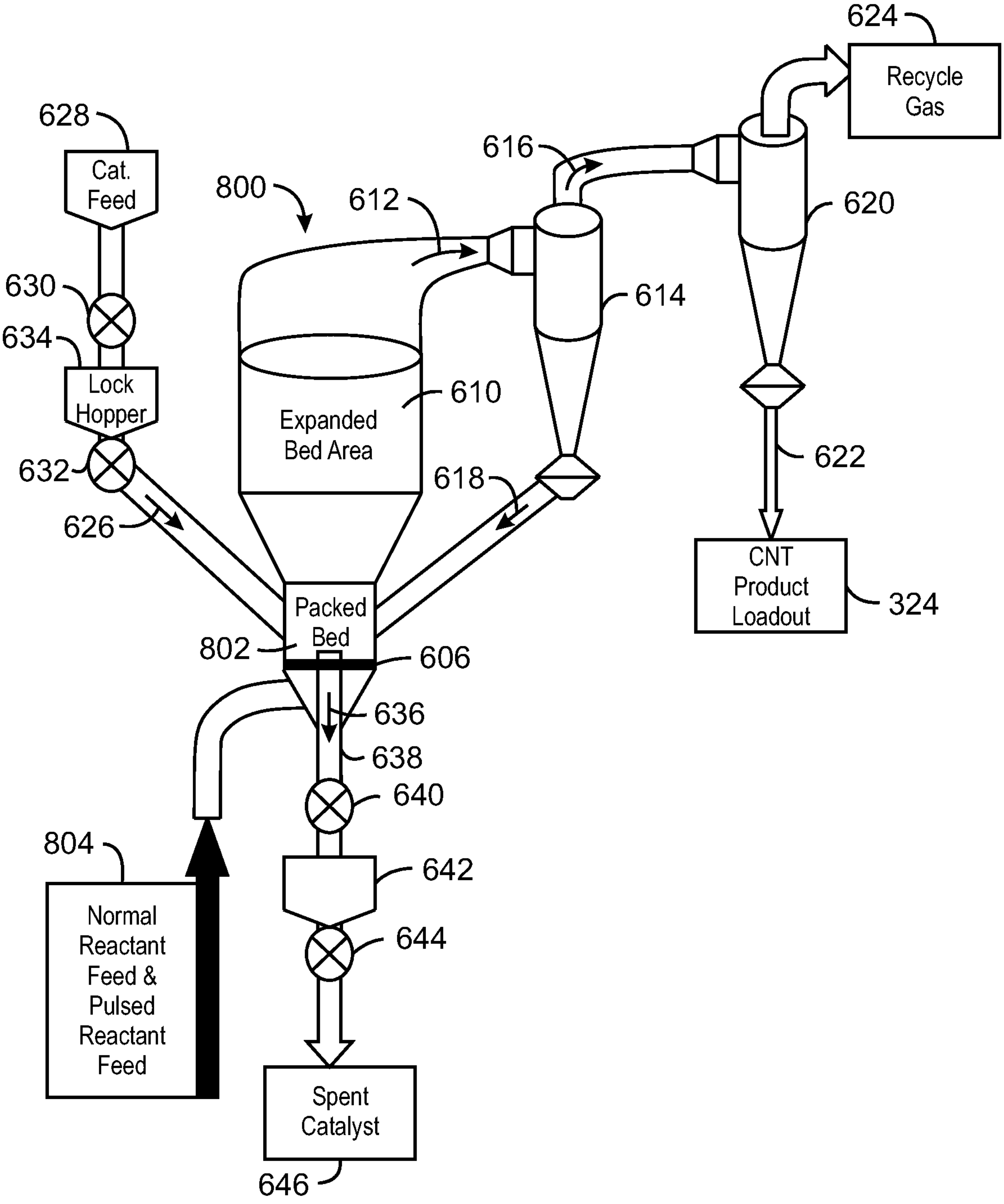
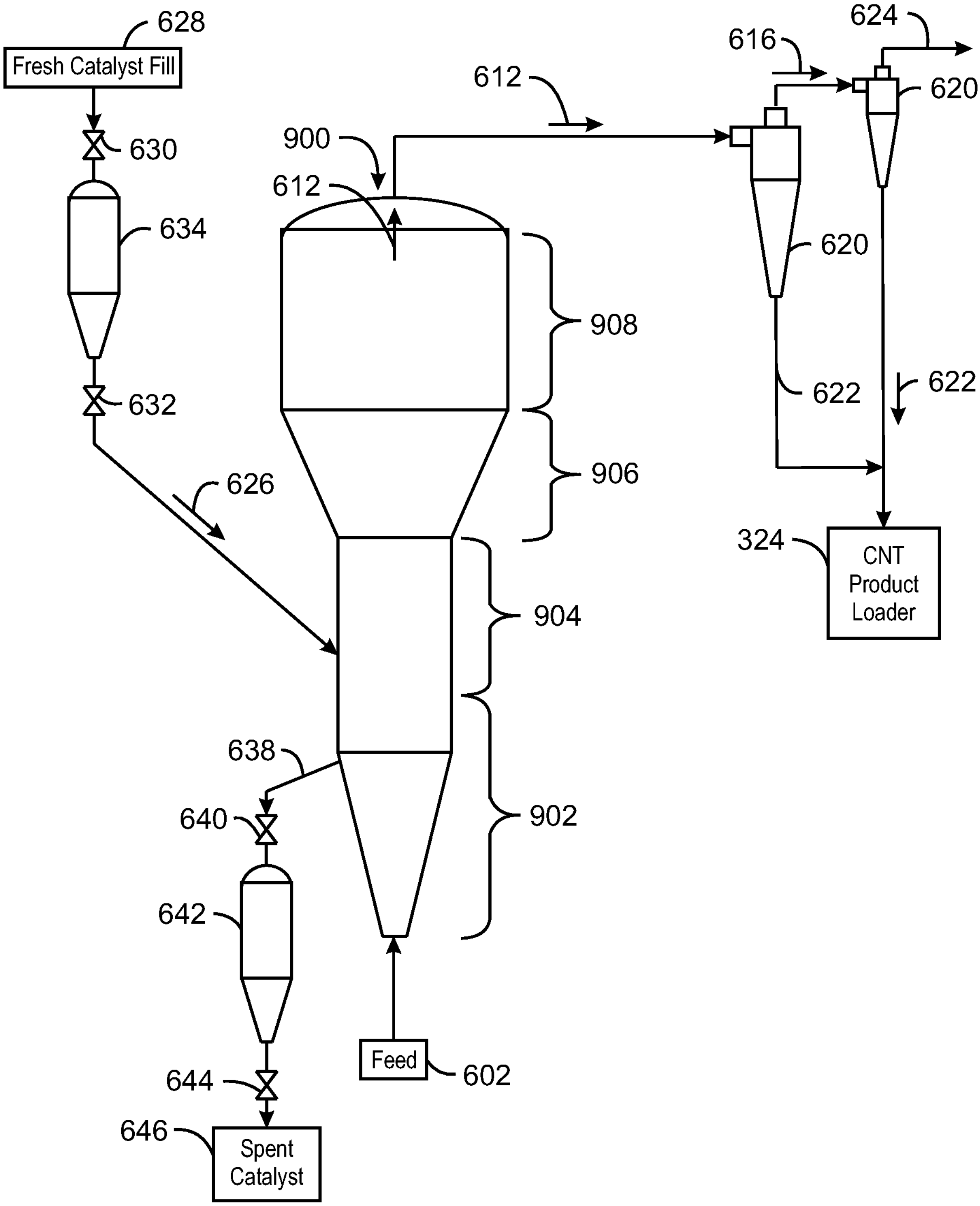

628
Cat. Feed
630
634
Lock Hopper
632
626
612
714
712
616
624
Recycle Gas
620
614
618
622
CNT Product Loadout
324
Fluid Bed
Reactor
704
702
708
Split Reactant Feed
706
710
700
Spent Catalyst
646

FIG. 7


624
Recycle Gas
628
Cat. Feed
616
800
612
620
630
614
634
Lock Hopper
Expanded Bed Area
610
632
618
622
626
CNT Product Loadout
324
Packed Bed
802
606
636
638
640
804
642
Normal Reactant Feed & Pulsed Reactant Feed
644
Spent Catalyst
646

800

FIG. 8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Fresh Catalyst Fill
630
634
632
626
900
612
612
908
906
904
902
638
640
642
644
646
Spent Catalyst
Feed
602
616
624
620
620
622
622
324
CNT Product Loader

900

FIG. 9

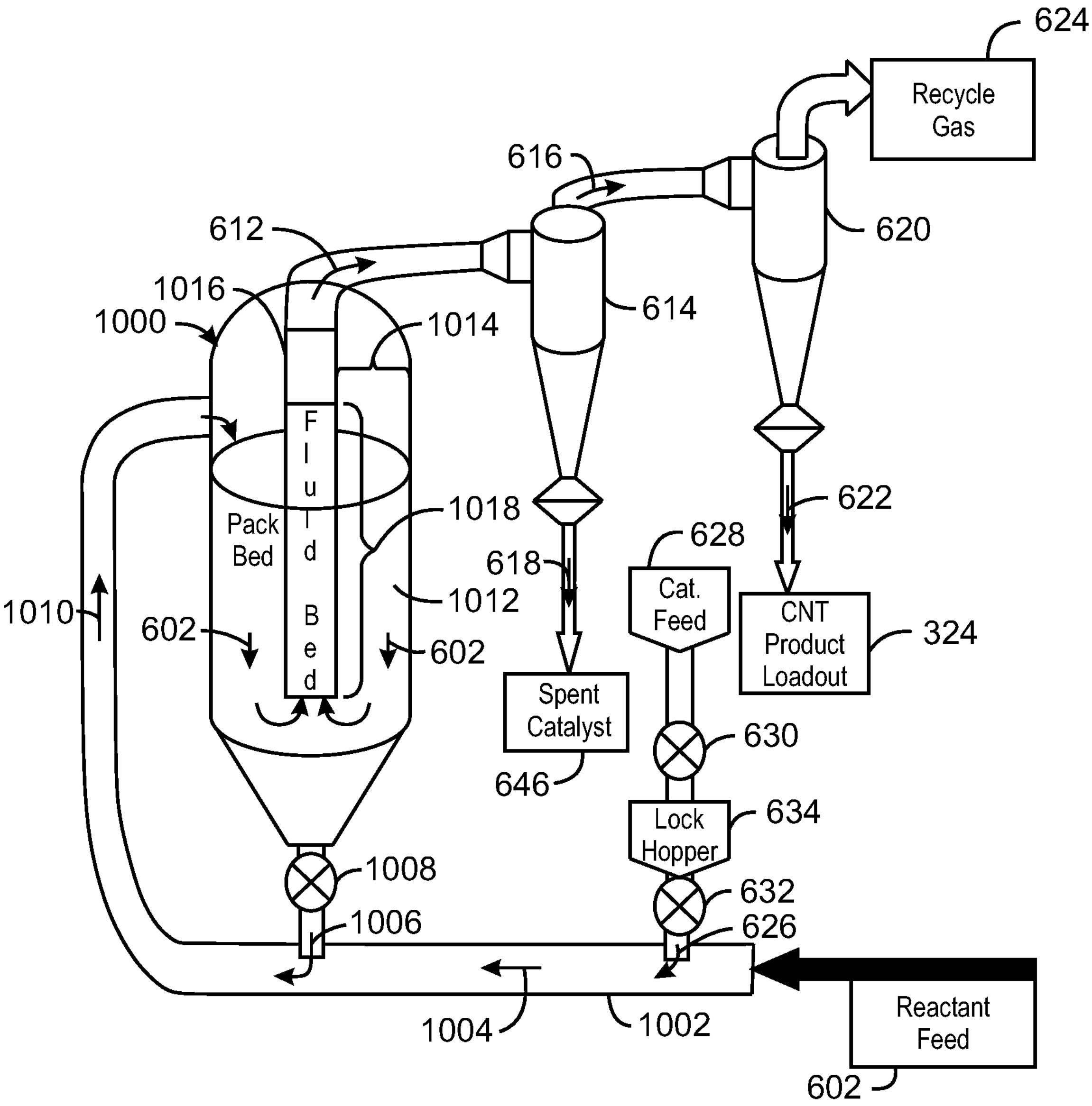
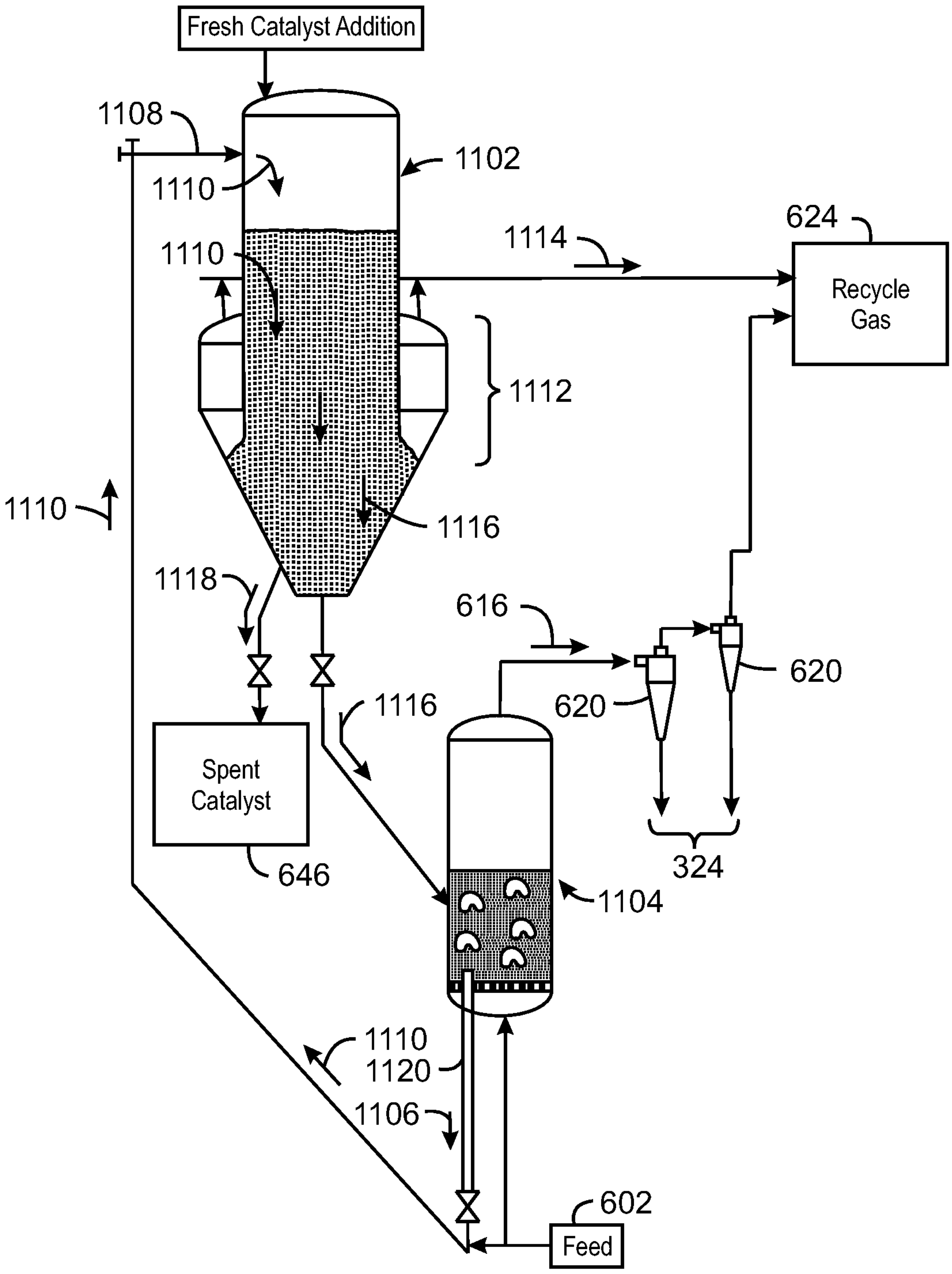

624
Recycle Gas
616
620
612
1016
614
1000
1014
F l u i d B e d
1018
Pack Bed
622
628
618
1012
Cat. Feed
CNT Product Loadout
1010
602
602
324
Spent Catalyst
630
646
634
Lock Hopper
1008
632
1006
626
1004
1002
Reactant Feed
602

FIG. 10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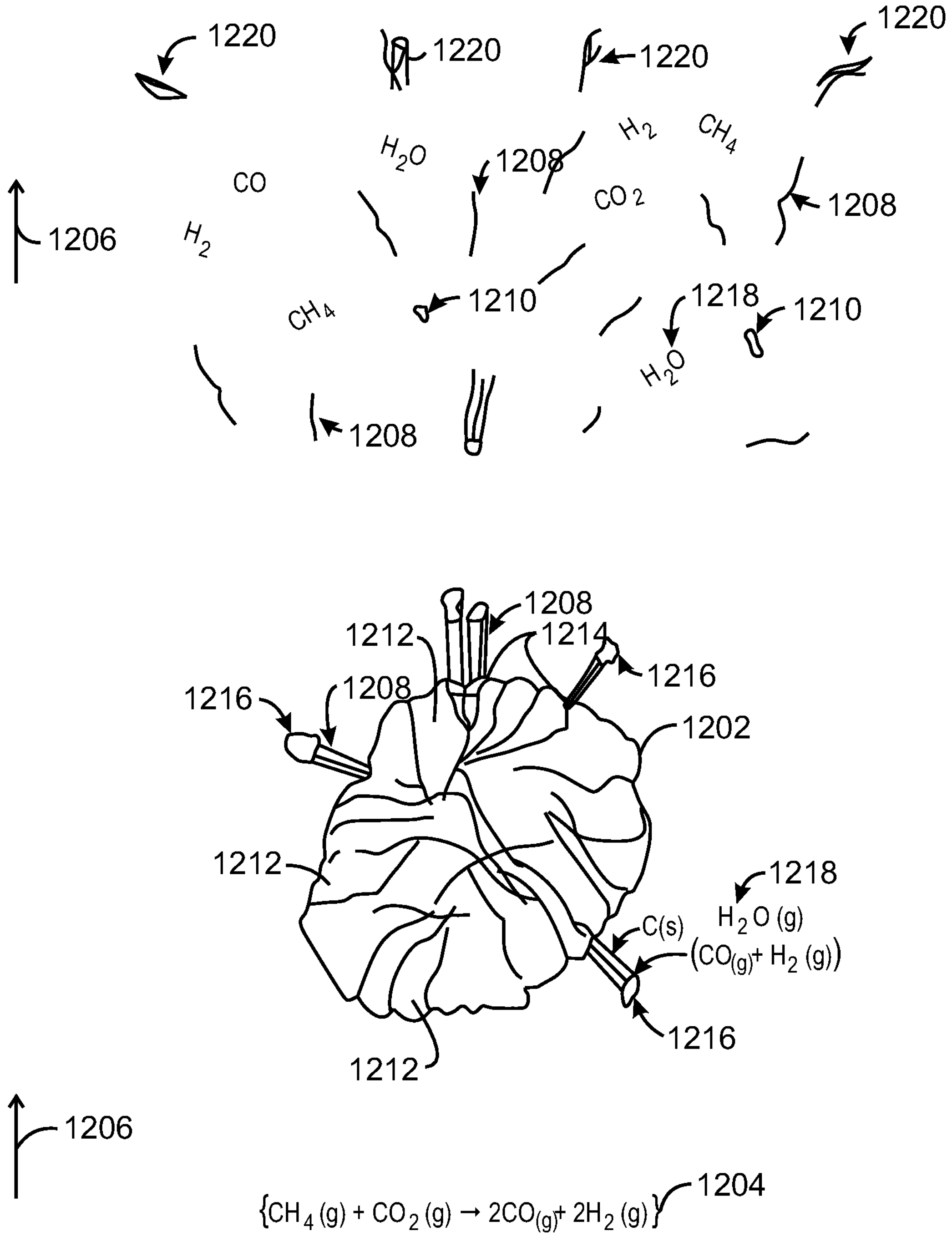
1108
1102
1110
1110
1114
624
Recycle Gas
1112
1110
1116
1118
616
620
620
1116
Spent Catalyst
646
324
1104
1110
1120
1106
602
Feed

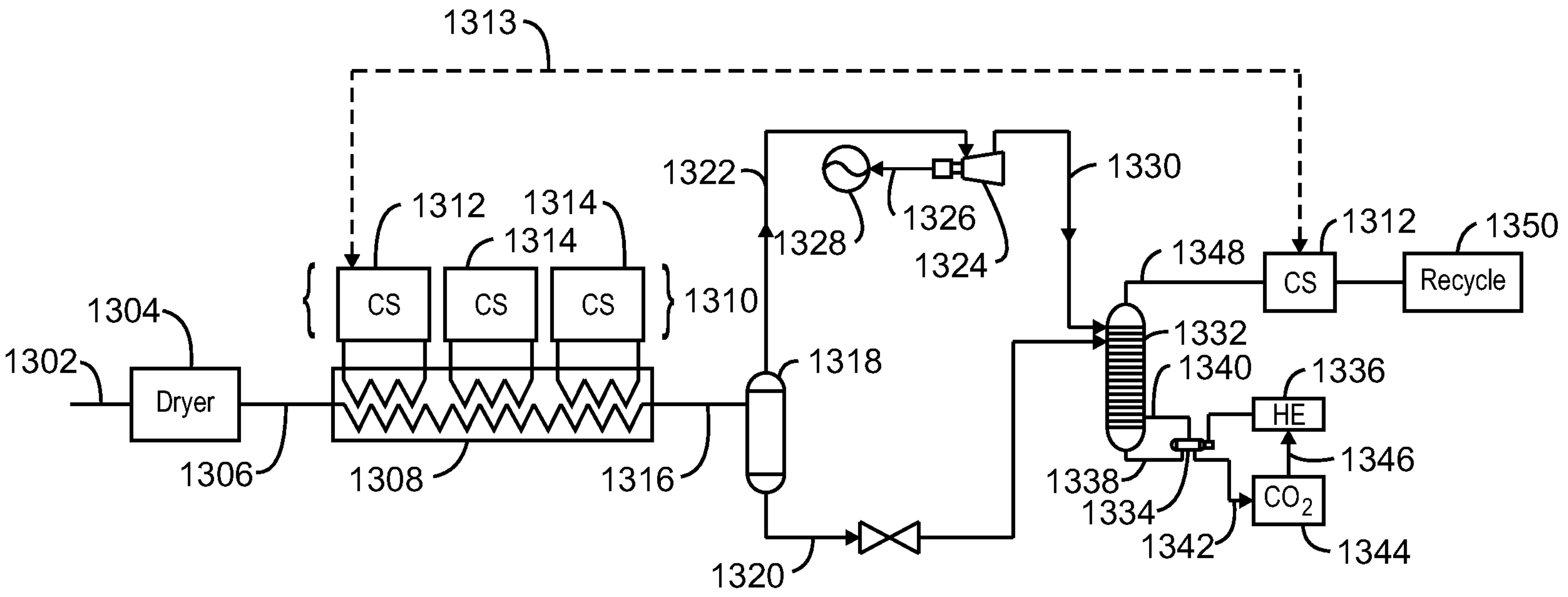
1100

FIG. 11


1220
1220
1220
1220
H_2O
H_2
CH_4
CO
1208
CO_2
1208
1206
H_2
CH_4
1210
1218
1210
H_2O
1208
1208
1212
1214
1216
1216
1208
1202
1212
1218
$H_2O(g)$
C(s)
$(CO_{(g)} + H_2(g))$
1216
1212
1206
$\{CH_4(g) + CO_2(g) \rightarrow 2CO_{(g)} + 2H_2(g)\}$
1204

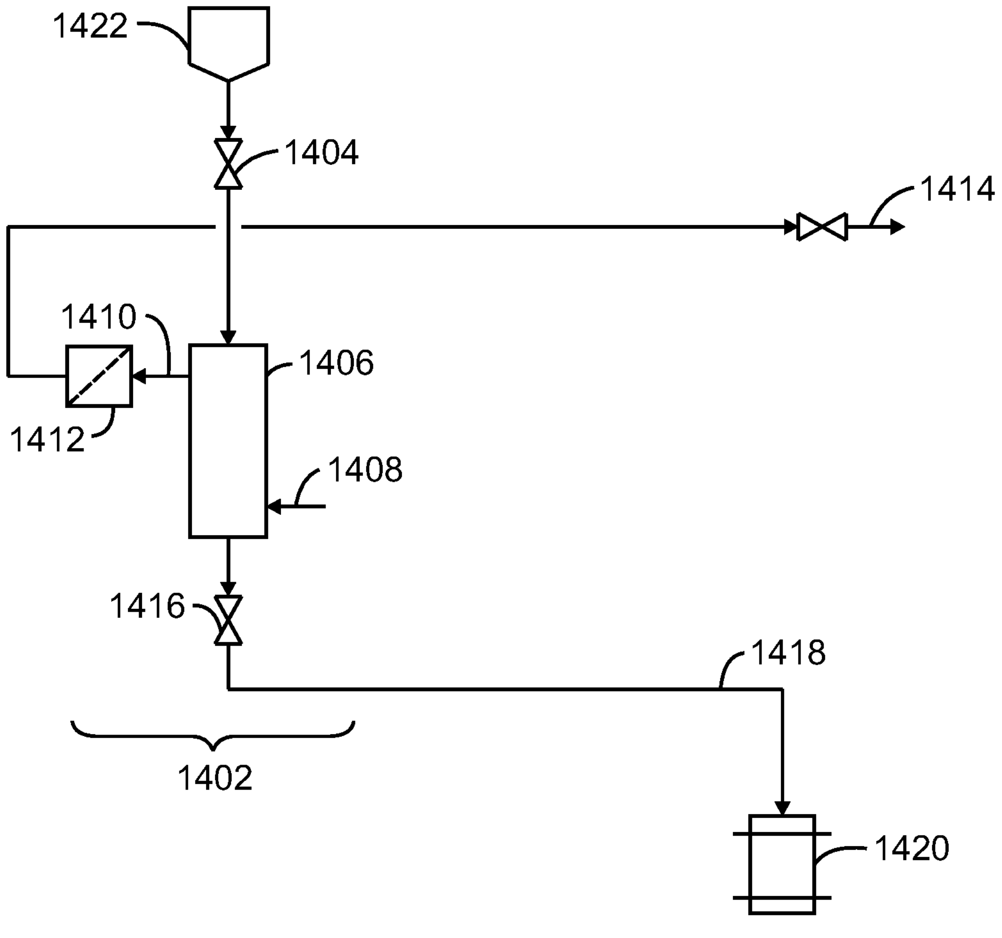
1200

FIG. 12


1313
1322
1330
1328
1326
1324
1312
1314
1314
1310
1304
1302
Dryer
CS
CS
CS
1318
1306
1308
1316
1320
1348
1312
CS
1350
Recycle
1332
1340
1336
HE
1338
1334
1346
1342
CO_2
1344

1300

FIG. 13



1400

FIG. 14

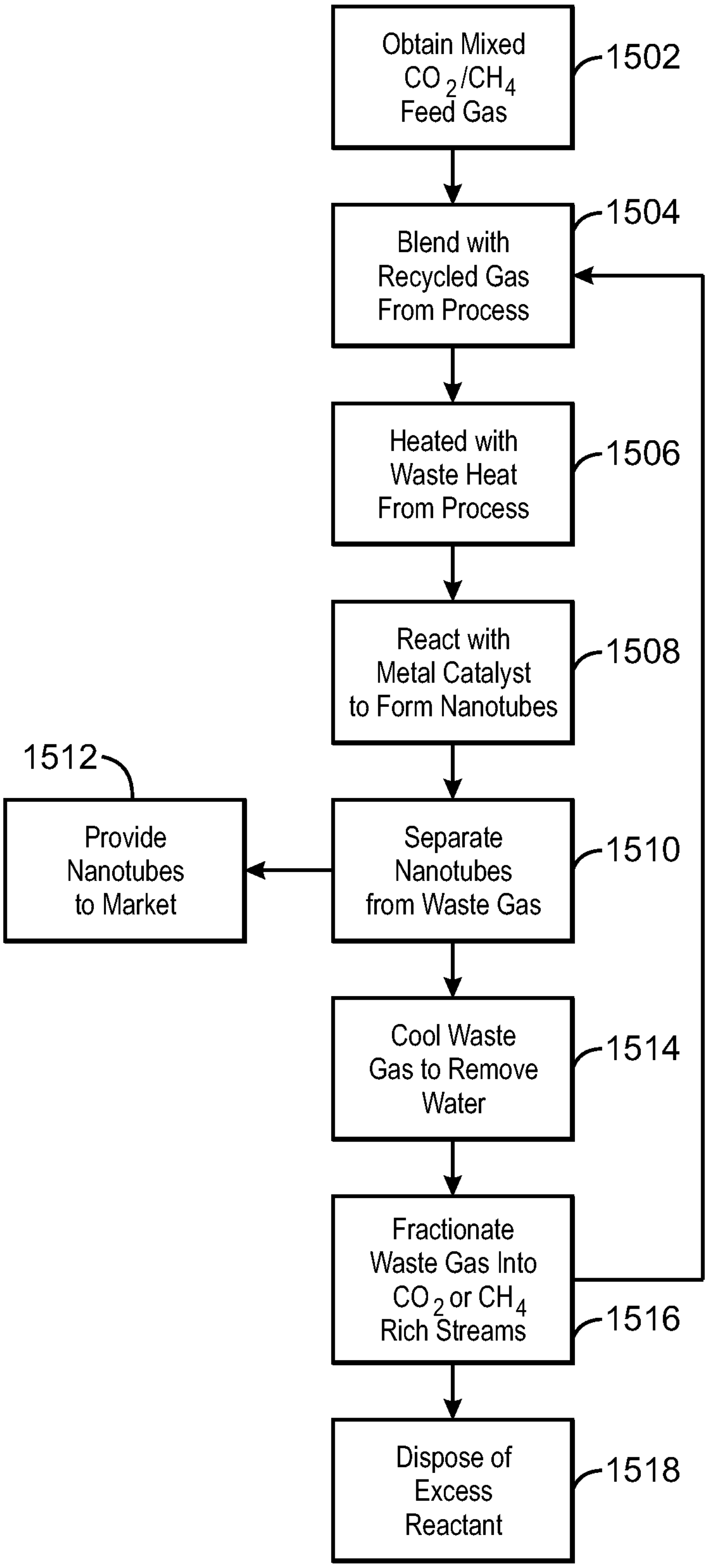

Obtain Mixed CO_2/CH_4 Feed Gas
1502
Blend with Recycled Gas From Process
1504
Heated with Waste Heat From Process
1506
React with Metal Catalyst to Form Nanotubes
1508
1512
Provide Nanotubes to Market
Separate Nanotubes from Waste Gas
1510
Cool Waste Gas to Remove Water
1514
Fractionate Waste Gas Into CO_2 or CH_4 Rich Streams
1516
Dispose of Excess Reactant
1518
1500

FIG. 15

INTERNATIONAL SEARCH REPORT

PCT/US2013/059613 24.01.2014

International application No.
PCT/US 13/59613

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C01B 31/02 (2014.01)
USPC - 423/445, 423/447.1, 447.3, 447.8, 448, 450, 453-454

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - C01B 31/02 (2014.01)
USPC - 423/445

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 423/447.1, 447.3, 447.8, 448, 450, 453-454

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Keywords: Bosch w3 (reaction* or process or reduction*); PA = EXXONMOBIL; INV = ((DENTON w2 ROBERT) or (KOVEAL w2 RUSSELL) or (NOYES w2 DALLAS) or (RING w2 TERRY)); Bosch and hydrogen and (carbon w2 dioxide) and nano*; hybrid w2 reactor*, expanding fluidized bed; staged fluidized bed; (expanding stages) and (fluidized bed); (pseudo* or fluidized)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2011/0085961 A1 (Noda et al.) 14 April 2011 (14.04.2011) Abstract, para [0029], [0037], [0039], [0064], [0065], [0075], [0078], [0083], [0090], [0091], [0097], [0102], [0124], Figure 1, 3	1-25, 27-29
Y	US 2012/0034150 A1 (Noyes) 9 February 2012 (09.02.2012) para [0006], [0007], [0078], [0104], [0137]	1-30
Y	US 2002/0131910 A1 (Resasco et al.) 19 September 2002 (19.09.2002) para [0060], [0066], [0073], [0075], [0076], Figures 2-5.	4, 5, 10-19, 24, 26-30

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier application or patent but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 05 January 2014 (05.01.2014)	Date of mailing of the international search report 24 JAN 2014
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774