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Systems and methods for hydrocarbon pyrolysis

Abstract

Systems for hydrocarbon pyrolysis are provided, which may comprise a reactor configured to contain a liquid metal; a heater operably coupled to the reactor to form a heating zone; a cooler operably coupled to the reactor to form a cooling zone; a gas delivery assembly comprising an inlet and configured to deliver a feed gas comprising a hydrocarbon as a plurality of bubbles through the liquid metal; an outlet configured to deliver a product gas to a separation assembly, the product gas formed from pyrolysis of the hydrocarbon in the liquid metal, the product gas comprising H.sub.2 and carbon; and the separation assembly configured to separate the carbon from other components of the product gas. The reactor is configured to entrain the carbon from pyrolysis of the hydrocarbon in the liquid metal into the product gas without accumulating the carbon in the interior chamber during pyrolysis.

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Background/Summary

BACKGROUND

(1) The pyrolytic conversion of methane to hydrogen and carbon (i.e., CH₄ (g) → 2H₂ (g) + C (s)) has the potential to provide an emission-free process for the production of hydrogen from a greenhouse gas. However, numerous challenges have hindered the commercial implementation of this process. For example, systems for non-catalytic methane pyrolysis require extreme operating temperatures. Solid metal catalysts may be used to allow for reduced operating temperatures but suffer from rapid carbon buildup (coking). Liquid metals and alloys facilitate thermal energy transfer needed for endothermic pyrolysis reaction and promote pyrolysis reaction rate, but separation of the carbon from the liquid metal/alloy remains a significant and unsolved problem.

SUMMARY

(2) The present disclosure provides a hydrocarbon pyrolysis system configured to entrain solid

carbon in a product gas produced from pyrolysis of a hydrocarbon in a liquid metal. Embodiments of the present systems achieve carbon entrainment in the product gas without accumulating carbon within a reactor of the system during pyrolysis. This allows for the continuous, uninterrupted production of hydrogen from the hydrocarbon, thereby increasing efficiency and reducing costs.

(3) In one aspect, systems for hydrocarbon pyrolysis are provided. In embodiments, a system for hydrocarbon pyrolysis comprises a reactor configured to contain a liquid metal within an interior chamber of the reactor; a heater operably coupled to the reactor to form a heating zone within a first portion of the interior chamber comprising the liquid metal; a cooler operably coupled to the reactor to form a cooling zone within a second portion of the interior chamber above the first portion; a gas delivery assembly comprising an inlet in fluid communication with the interior chamber, the gas delivery assembly configured to deliver a feed gas comprising a hydrocarbon as a plurality of bubbles through the liquid metal; an outlet in fluid communication with the interior chamber and configured to deliver a product gas to a separation assembly, the product gas formed from pyrolysis of the hydrocarbon in the liquid metal, the product gas comprising H₂ and carbon; and the separation assembly in fluid communication with the interior chamber via the outlet, the separation assembly configured to separate the carbon from other components of the product gas. The reactor is configured to entrain the carbon from pyrolysis of the hydrocarbon in the liquid metal into the product gas without accumulating the carbon in the interior chamber during pyrolysis.

(4) In embodiments, a system for hydrocarbon pyrolysis comprises a reactor configured to contain a liquid metal within an interior chamber of the reactor; a heater operably coupled to the reactor to form a heating zone within a first portion of the interior chamber comprising the liquid metal; a cooler operably coupled to the reactor to form a cooling zone within a second portion of the interior chamber above the first portion; a gas delivery assembly comprising an inlet in fluid communication with the interior chamber, the gas delivery assembly configured to deliver a feed gas comprising a hydrocarbon as a plurality of bubbles through the liquid metal; an outlet in fluid communication with the interior chamber and configured to deliver a product gas to a separation assembly, the product gas formed from pyrolysis of the hydrocarbon in the liquid metal, the product gas comprising H₂ and carbon; and the separation assembly in fluid communication with the interior chamber via the outlet, the separation assembly configured to separate the carbon from other components of the product gas. The system does not comprise any other outlet through which carbon exits the interior chamber other than the outlet configured to deliver the product gas to the separation assembly.

(5) In embodiments, a system for hydrocarbon pyrolysis comprises a reactor configured to contain a liquid metal within an interior chamber of the reactor; a heater operably coupled to the reactor to form a heating zone within a first portion of the interior chamber comprising the liquid metal; a cooler operably coupled to the reactor to form a cooling zone within a second portion of the interior chamber above the first portion; a gas delivery assembly comprising an inlet in fluid communication with the interior chamber, the gas delivery assembly configured to deliver a feed gas comprising a hydrocarbon as a plurality of bubbles through the liquid metal; an outlet in fluid communication with the interior chamber and configured to deliver a product gas to a separation assembly, the product gas formed from pyrolysis of the hydrocarbon in the liquid metal, the product gas comprising H₂ and carbon; the separation assembly in fluid communication with the interior chamber via the outlet, the separation assembly configured to separate the carbon from other components of the product gas; and a controller comprising a processor and a non-transitory computer-readable medium operably coupled to the processor, the non-transitory computer-readable medium comprising instructions, that, when executed by the processor, cause the system to adjust one or more of a feed gas flow rate, a reactor temperature, and a reactor pressure to achieve a linear gas velocity of at least about 5 cm/s through the interior chamber.

(6) In another aspect, processes for hydrocarbon pyrolysis are provided. In embodiments, a process

for hydrocarbon pyrolysis comprises delivering a feed gas comprising a hydrocarbon to a reactor configured to contain a liquid metal within an interior chamber of the reactor under conditions to induce pyrolysis of the hydrocarbon in the liquid metal to form a product gas comprising H₂ and carbon. The feed gas is delivered at a linear gas velocity through the interior chamber such that the carbon is entrained into the product gas without accumulating the carbon in the interior chamber during pyrolysis.

(7) Other principal features and advantages of the disclosure will become apparent to those skilled in the art upon review of the following drawings, the detailed description, and the appended claims.

Description

BRIEF DESCRIPTION OF THE DRAWINGS

(1) Illustrative embodiments of the disclosure will hereafter be described with reference to the accompanying drawings.

(2) FIG. 1 shows a cross-sectional view of a schematic illustration of a hydrocarbon pyrolysis system according to an illustrative embodiment.

(3) FIG. 2 shows a plot of upstream and downstream pressures in an alumina tube reactor filled with molten zinc while flowing nitrogen (N₂) through the reactor at a gas flow rate of 70 sccm.

(4) FIG. 3 shows a plot of upstream and downstream pressures in an alumina tube reactor filled with molten zinc while flowing methane (CH₄) and N₂ through the reactor at a gas flow rate of 70 sccm (60 sccm CH₄ and 10 sccm N₂). The upstream pressure starts to increase after about 4 hours, demonstrating the problem of carbon accumulation in the reactor.

(5) FIG. 4 shows a plot of upstream and downstream pressures in an alumina tube reactor filled with molten zinc while flowing CH₄ and N₂ through the reactor at a gas flow rate of 70 sccm (60 sccm CH₄ and 10 sccm N₂), but periodically increasing the flow of N₂ through the reactor to 510 sccm. This periodic increase in gas flow rate periodically increases the linear gas velocity in the reactor, demonstrating that linear gas velocity may be adjusted to prevent the accumulation of carbon within the reactor, including so that no carbon accumulates within the reactor.

(6) FIG. 5 shows a block diagram of a hydrocarbon pyrolysis system according to an illustrative embodiment, including an illustrative controller which may be used to control various components of the system.

DETAILED DESCRIPTION

(7) Systems for carrying out hydrocarbon pyrolysis in liquid metal are provided. In the present disclosure, “hydrocarbon pyrolysis” refers to breaking down a hydrocarbon into H₂ and carbon (e.g., CH₄ (g) → H₂ (g) + C (s)) using an elevated temperature, a catalyst, or both. A cross-sectional view of a schematic of an illustrative system **100** is shown in FIG. 1. The system **100** comprises a reactor **102**, the component within which the relevant chemical reactions take place. The reactor **102** is in the form of a cylindrical column having a top end **104**, a bottom end **106** opposite the top end **104**, and a side wall **108** between the top **104** and bottom **106** ends, together which define an interior chamber **110** which may be partially filled with a liquid metal **112**. (Under the operating conditions of the system **100**, the metal **112** is in its liquid form, but it is understood that outside of such operating conditions, the metal **112** may be in its solid form or its gaseous form. Both the terms “liquid” and “molten” may be used to refer to a metal in its liquid phase. Thus, “liquid metal” and “molten metal” may be used interchangeably.) A heater **114** is operably coupled to a portion of the reactor **102** so as to form a heating zone **116** within the interior chamber **110**. A cooler **118** is operably coupled to another, different portion of the reactor **102** so as to form a cooling zone **120** within the interior chamber **110**. Generally, the heating zone **116**

encompasses the volume of the liquid metal **112** within the interior chamber **110** while the cooling zone **120** encompasses the atmosphere within the interior chamber **110** above the liquid metal **112**. (8) A feed gas **121** enters the reactor **102** through an inlet **122** positioned at or near the bottom end **106** of the reactor **102**. The inlet **122** is fluidly connected to one or more spargers (or the like) **124** configured to deliver the feed gas **121** to the liquid metal **112** as a plurality of bubbles **126**. The inlet **122** and the spargers (or the like) may be part of a gas delivery system operably coupled to the reactor **102**. The feed gas **121** comprises the desired hydrocarbon (e.g., methane). Decomposition of the hydrocarbon to produce H₂ and carbon via pyrolysis occurs as the bubbles **126** travel through the liquid metal **112**, generally upwardly toward an interface **128** formed between the liquid metal **112** and the overlying atmosphere in the cooling zone **120**. The upward flow of bubbles through the liquid metal **112** in the reactor **102** distinguishes the system **100** from other types of reactors, e.g., liquid mist reactors; i.e., reactor **102** is not a liquid mist reactor. Pyrolysis occurring in the liquid metal **112** results in a product gas **127** being released from the interface **128** and into the atmosphere of the cooling zone **120**. This is illustrated schematically in FIG. 1 with the bursting bubble **151** about to release carbon from within the bursting bubble. The flow of the bubbles **126** and the product gas **127** is indicated by the arrow **150** in FIG. 1. The arrow **150** also provides a reference point for upstream and downstream positions in the system **100**, as labeled in FIG. 1. The product gas **127** comprises the H₂ gas, carbon, and generally, at least some unreacted hydrocarbon. Some metal of the liquid metal **112** may also be present in the product gas **127**, either as metal vapor, or as liquid droplets or solid adsorbed on surfaces of the carbon, or both. (9) The product gas **127** exits the reactor **102** through an outlet **130** positioned at or near the top end **104** of the reactor **102**. At least some heat is removed from the product gas **127** as it travels through the cooling zone **120** prior to exiting through the outlet **130**. In embodiments, sufficient heat is removed so that metal vapor that may be present in the product gas **127** condenses and flows back down into the heating zone **116** of the reactor **102** and to the liquid metal **112** therein. This temperature drop in the product gas **127** in the cooling zone **120** leads to a decrease in metal vapor pressure and an increase in the amount of metal vapor condensed and returned to the liquid metal **112**.

(10) The system **100** further includes a separation assembly **132** in fluid communication with the reactor **102** via the outlet **130**. The separation assembly **132** is configured to separate individual components of the product gas **127** from one another, e.g., to separate out the H₂ from the product gas **127** and to separate out the carbon from the product gas **127**. In embodiments, such as in the system **100**, the separation assembly **132** is also configured to separate out liquid/solid metal that may be present in the product gas **127** and return it to the reactor **102** via a first recirculation path **134**. However, other embodiments need not include this feature or the first recirculation path **134**, i.e., it is optional. In embodiments, such as in the system **100**, the separation assembly **132** is also configured to separate out unreacted hydrocarbon that may be present in the product gas **127** and return it to the reactor **102** via a second recirculation path **136**. The separation assembly **132** may include components configured to achieve the separations described above, e.g., filters, pressure swing adsorption units, gravimetric separators, cyclone separators, electrostatic separators, and evaporation units.

(11) Other components may be included in system **100**. One or more pressure gauges may be included to measure the pressure in the reactor **102**. For example, the system **100** may include a downstream pressure gauge positioned at a downstream position relative to the inlet **122**, e.g., at or near the outlet **130**. The downstream pressure gauge may be used to measure the pressure of the product gas **127**. The system **100** may include an upstream pressure gauge positioned at an upstream position, e.g., at or near the inlet **122**. The upstream pressure gauge may be used to measure the pressure of the feed gas **121**. As further described below, the pressure of the feed gas **121** (e.g., as measured from an upstream pressure gauge) may be used to provide an indication of carbon accumulation within the reactor **102**. Specifically, an increase in upstream pressure indicates

carbon accumulation and no change in upstream pressure indicates no increase in carbon accumulation. Similarly, one or more temperature sensors may be included in the system **100**. One or more gas flow controllers may be included in the system **100** e.g., to provide a desired flow rate of the feed gas **121**.

(12) Referring back to the reactor **102**, the reactor **102** may be configured to achieve a linear gas velocity through interior chamber **110** of the reactor **102** that prevents carbon accumulation therein, including so that no carbon accumulates within the reactor. The phrase “linear gas velocity” may be referred to as “superficial gas velocity.” Although some existing pyrolysis systems have considered carbon entrainment, the present disclosure is based, in part, on the unexpected discovery that linear gas velocity can be tuned to prevent carbon accumulation altogether, including so that no carbon accumulates within the reactor. By contrast, existing pyrolysis systems do not preclude carbon accumulation, including carbon accumulating in the form of a layer or slag at the interface **128**. Thus, existing pyrolysis systems require additional components to remove carbon, such as scrapers or the like to mechanically remove the carbon (and generally some of the liquid metal) from the reactor, as well as an additional outlet to remove the carbon.

(13) As noted above, carbon accumulation within the reactor **102** may be indicated by measuring an upstream pressure (e.g., from an upstream pressure gauge measuring the pressure of the feed gas **121**) and a downstream pressure (e.g., from a downstream pressure gauge measuring the pressure of the product gas **127**). An increase in upstream pressure with no change in downstream pressure during operation (i.e., during pyrolysis) of the reactor **102** is an indication of carbon accumulation. (See FIG. 3.) By contrast, no change in upstream pressure and no change in downstream pressure during operation of the reactor **102** is an indication of no carbon accumulation. (See FIG. 4.) By “no change” it is meant that the pressure during operation (as feed gas **121** is flowing through the reactor **102**) is within 10% of an initial pressure (time=0). This includes within 5%, within 2%, and within 1%. By way of illustration, if an initial upstream pressure at time=0 is 30 psig, no change in upstream pressure during reactor operation means that the upstream pressure remains within 10% (or 5%, 2%, 1%) of 30 psig during reactor operation. Similarly, if an initial downstream pressure at time=0 is 30 psig, no change in downstream pressure during reactor operation means that the downstream pressure remains within 10% (or 5%, 2%, 1%) of 30 psig during reactor operation. Thus, upstream pressures and downstream pressures that each remain within 10% (or 5%, 2%, 1%) of their respective values during pyrolysis indicate that the carbon is being entrained into the product gas without accumulating the carbon within the reactor **102**.

(14) The linear gas velocity through the reactor **102** may be calculated from Equation 1 (see also, the Example, below):

$$(15) \quad \frac{F(\text{cm}^3 / \text{s})}{A(\text{cm}^2)} * \left(\frac{T_{\text{reactor}}(\text{K})}{P_{\text{reactor}}(\text{psia})} * \frac{P_{\text{standard}}(\text{psia})}{T_{\text{standard}}(\text{K})} \right) \quad (\text{Equation 1})$$

wherein F is the feed gas flow rate in cm³/s at standard temperature and pressure, A is the reactor cross-sectional area, T_{sub reactor} is the reactor temperature, P_{sub reactor} is the reactor pressure, P_{sub standard} is standard pressure (14.7 psia), and T_{sub standard} is standard temperature (273.15 K). Thus, the linear gas velocity depends upon the reactor geometry (cross-sectional area A of the interior chamber **110**) and reactor conditions (feed gas flow rate, reactor temperature, reactor pressure).

(16) In embodiments, the reactor **102** is configured to achieve a linear gas velocity of at least 5 cm/s at a feed gas flow rate of 300 sccm (standard cubic centimeter per second) or higher (including a feed gas flow rate of 300 sccm), a reactor temperature of 1,000° C., and a reactor pressure of 147 psia. This includes achieving a linear gas velocity of at least 10 cm/s or at least 25 cm/s at this feed gas flow rate, this reactor temperature, and this reactor pressure. This means that at a reactor temperature of 1,000° C., a reactor pressure of 147 psia, and a feed gas flow rate of 300 sccm or higher (including a feed gas flow rate of 300 sccm), the linear gas velocity of the reactor **102** is 5 cm/s or higher (or 10 cm/s or higher or 25 cm/s or higher). In embodiments, the reactor

102 is configured to achieve a linear gas velocity of no more than 100 cm/s at a feed gas flow rate of 2,000,000 sccm or lower (including a feed gas flow rate of 2,00,000 sccm), a reactor temperature of 1,000° C., and a reactor pressure of 147 psia. This includes achieving a linear gas velocity of no more than 80 cm/s or no more than 50 cm/s at this feed gas flow rate, this reactor temperature, and this reactor pressure. This means that at a reactor temperature of 1,000° C., a reactor pressure of 147 psia, and a feed gas flow rate of 2,000,000 sccm or lower (including a feed gas flow rate of 2,000,000 sccm), the linear gas velocity of the reactor **102** is 100 cm/s or less (or 80 cm/s or less or 50 cm/s or less). In embodiments, at a reactor temperature of 1,000° C., a reactor pressure of 147 psia, and a flow rate of between 300 sccm and 2,000,000 sccm, the linear gas velocity of the reactor **102** is between 5 cm/s and 100 cm/s (or between 10 cm/s and 80 cm/s or between 25 cm/s and 50 cm/s). Reactors configured to achieve these linear gas velocities at these feed gas flow rates, reactor temperatures, and reactor pressures (and thus, reactors configured to achieve carbon entrainment without accumulating carbon) may be obtained by using an appropriate minimum cross-sectional area A for the reactor **102**. As further described below, during operation of the reactor **102** (or any given reactor), adjustments may be made to feed gas flow rate, reactor temperature, reactor pressure, or combinations thereof, to ensure these linear gas velocities are met.

(17) Referring back to FIG. 1, it is noted that the system **100** does not comprise any other inlet other than inlet **122**. In embodiments, the present systems need not comprise any other inlet through which a gas enters the reactor other than an inlet (e.g., inlet **122**) configured to deliver a feed gas to the reactor. However, in embodiments, the system **100** further comprises a carrier gas inlet configured to deliver a carrier gas to the cooling zone **120** of the reactor **102**. The carrier gas inlet may be positioned along a side wall **108** within the cooling zone **120**. Delivery of the carrier gas in this way is useful to further reduce the temperature in the cooling zone **120** and promote condensation of metal vapor that may be present in the product gas **127** and its return to the liquid metal **112** in the heating zone **116**. The carrier gas may comprise methane, hydrogen, and nitrogen. In embodiments, the present systems do not comprise any other inlet other than inlet **122** and optionally, a carrier gas inlet.

(18) It is further noted that the system **100** does not comprise any other outlet other than outlet **130**. In embodiments, the present systems need not comprise any other outlet through which carbon exits the reactor other than an outlet (e.g., outlet **130**) configured to deliver a product gas to a separation assembly (e.g., separation assembly **132**). The system **100** does not comprise components for physically removing carbon from the interface **128** (other than the product gas flow-driven carbon entrainment described herein). These features are all because the system **100** is able to achieve carbon entrainment in the product gas **127** with no carbon accumulation within the reactor **102**.

(19) Various metals may be used to provide a liquid metal for use with any of the present systems, including system **100**. A single type (i.e., a single element) of metal may be used, or a combination of different types of metals (i.e., a metal alloy which is a combination of different elements) may be used. Thus, unless otherwise indicated, “metal” encompasses “metal alloy.” In embodiments, the metal is one having a relatively low boiling point, e.g., no more than 1200° C. Illustrative metals include zinc, gallium, tin, aluminum, lead, bismuth, tellurium, and copper. In embodiments, the liquid metal comprises or consists of zinc. In embodiments, the liquid metal does not comprise a molten salt and does not comprise a solid metal catalyst. In embodiments, the liquid metal consists of a single liquid phase, i.e., as opposed to multiple liquid phases. In embodiments, the liquid metal consists of a single type of metal.

(20) Various hydrocarbons may be used in a feed gas being processed by any of the present systems, including system **100**. A single type (i.e., a single chemical compound) of hydrocarbon may be used in the feed gas, or a mixture of different types (i.e., different chemical compounds) of hydrocarbons may be used. In embodiments, the hydrocarbon (hydrocarbon mixture) is one having a relatively low boiling point, e.g., no more than 500° C., no more than 400° C., or no more than

300° C. Otherwise, the hydrocarbon is not particularly limited, but may be an alkane, an alkene, an alkyne, or an arene. The hydrocarbon may be linear, branched, or cyclic. Illustrative hydrocarbons include methane, propane, butane, pentane, hexane, benzene, xylene, and toluene. Illustrative hydrocarbon mixtures include natural gas, liquified petroleum gas, gasoline, diesel, kerosene, naphtha, and jet fuel (e.g., JP-8). These hydrocarbons and hydrocarbon mixtures may be used alone or in any combination. In embodiments, the hydrocarbon is methane or natural gas (hydrocarbon mixture).

(21) The carbon produced by any of the present systems, including system **100**, refers to carbon in its solid form. However, the particular solid form is not limited, but may be carbon black, carbon fiber, carbon nanofiber, carbon nanotube, carbon nanocage, fullerene, graphite, amorphous carbon, coke, needle coke, or diamond. The carbon may include one or more of these solid forms.

(22) The conditions under which the pyrolysis is carried out using any of the present systems, including system **100**, include parameters such as linear gas velocity, flow rate of a feed gas, reactor temperature, and reactor pressure. Referring to system **100**, as described above, the linear gas velocity is generally selected to prevent carbon accumulation within the reactor **102**, including so that no carbon accumulates within the reactor **102**. (The indication of carbon accumulation has been described above.) This can include increasing the flow rate of the feed gas **121** for a selected cross-sectional area A of the reactor **102**, a selected reactor temperature and a selected reactor pressure. However, adjustments to one or more of the flow rate of the feed gas **121**, the reactor temperature, and the reactor pressure may be made to prevent carbon accumulation, including so that no carbon accumulates within the reactor. Illustrative linear gas velocities include those in a range of from 5 cm/s to 100 cm/s, from 10 cm/s to 80 cm/s, and from 25 cm/s to 60 cm/s. Illustrative feed gas **121** flow rates include those in a range of from 300 sccm to 2,000,000 sccm, from 1000 sccm to 1,000,000 sccm, from 5,000 sccm to 500,000 sccm, and from 10,000 sccm to 100,000 sccm. The reactor temperature may refer to the temperature of a heating zone, e.g., the heating zone **116** of the system **100**, which may be, e.g., in a range of from 500° C. to 1500° C., from 600° C. to 1400° C., or from 700° C. to 1300° C. (The reactor temperature/temperature of the heating zone may be considered to be the temperature of a liquid metal in the heating zone, e.g., the liquid metal **112**.) The reactor pressure may refer to either the upstream pressure or the downstream pressure as measured from upstream or downstream pressure gauges as described above. The reactor pressure may be in a range of from greater than atmospheric pressure to 20 bar, from 2 bar to 20 bar, or from 5 bar to 20 bar. The conditions under which pyrolysis is carried out may also refer to a temperature of a cooling zone, e.g., the cooling zone **120** of the system **100**, which may be, e.g., in a range of from 100° C. to 1300° C.

(23) The present disclosure also provides processes for hydrocarbon pyrolysis. In embodiments, such a process comprises delivering a feed gas comprising a hydrocarbon to a reactor configured to contain a liquid metal within an interior chamber of the reactor under conditions to induce pyrolysis of the hydrocarbon in the liquid metal to form a product gas comprising H₂ and carbon. The feed gas is delivered at a linear gas velocity through the interior chamber such that the carbon is entrained into the product gas without accumulating the carbon in the interior chamber during pyrolysis. (The indication of carbon accumulation by pressure measurement has been described above.) Any of the linear gas velocities disclosed herein may be used. Any of the pyrolysis conditions disclosed herein may be used.

(24) The hydrocarbon pyrolysis process may be carried out using any of the present systems. In embodiments, a process for hydrocarbon pyrolysis is carried out using system **100** (but any of the present systems may be used). Such a process may comprise delivering the feed gas **121** via the inlet **122** under conditions (see above) to induce pyrolysis of the hydrocarbon in the liquid metal **112** as the feed gas **121** moves upwardly through the liquid metal **112** to form the product gas **127**; and delivering the product gas **127** to the separation assembly **132** via the outlet **130**. The process may further comprise separating the carbon from other components of the product gas **127** in the

separation assembly **132**. In embodiments, the feed gas **121** is delivered at a linear gas velocity such that no carbon accumulates within the reactor **102**. (The indication of carbon accumulation by pressure measurement has been described above.) Any of the linear gas velocities disclosed herein may be used. Any of the pyrolysis conditions disclosed herein may be used. In embodiments, the process further comprises adjusting one or more of the feed gas flow rate, reactor temperature, reactor pressure in order to maintain a desired linear gas velocity (so as to ensure no carbon accumulation) during pyrolysis. In embodiments, the process further comprises adjusting one or more of the feed gas flow rate, reactor temperature, reactor pressure in order to maintain no change in pressure at an upstream pressure gauge and no change in pressure at a downstream pressure gauge (so as to ensure no carbon accumulation) during pyrolysis. In embodiments, the process further comprises condensing vaporized liquid metal in the cooling zone **120** for its return to the liquid metal **112**. In embodiments, the liquid metal **112** consists of zinc. In embodiments, the feed gas **121** comprises methane.

(25) Referring back to the present systems, including system **100**, any of the present systems may include a controller configured to control one or more components of the system. The controller may be integrated into the system as part of a single device or its functionality may be distributed across one or more devices that are connected to other system components directly or through a network that may be wired or wireless. A database, a data repository for the system, may also be included and operably coupled to the controller.

(26) Such a controller may include an input interface, an output interface, a communication interface, a computer-readable medium, a processor, and an application. The controller may be a computer of any form factor including an electrical circuit board.

(27) The input interface provides an interface for receiving information into the controller. Input interface may interface with various input technologies including, e.g., a keyboard, a display, a mouse, a keypad, etc. to allow a user to enter information into the controller or to make selections presented in a user interface displayed on the display. Input interface further may provide the electrical connections that provide connectivity between the controller and other components of the system.

(28) The output interface provides an interface for outputting information from the controller. For example, output interface may interface with various output technologies including, e.g., the display or a printer for outputting information for review by the user. Output interface may further provide an interface for outputting information to other components of the system.

(29) The communication interface provides an interface for receiving and transmitting data between devices using various protocols, transmission technologies, and media. Communication interface may support communication using various transmission media that may be wired or wireless. Data and messages may be transferred between the controller, the database, other components of the system and/or other external devices using communication interface.

(30) The computer-readable medium is an electronic holding place or storage for information so that the information can be accessed by the processor of the controller. Computer-readable medium can include any type of random access memory (RAM), any type of read only memory (ROM), any type of flash memory, etc. such as magnetic storage devices, optical disks, smart cards, flash memory devices, etc.

(31) The processor executes instructions. The instructions may be carried out by a special purpose computer, logic circuits, or hardware circuits. Thus, the processor may be implemented in hardware, firmware, or any combination of these methods and/or in combination with software. The term “execution” is the process of running an application or the carrying out of the operation called for by an instruction. The instructions may be written using one or more programming language, scripting language, assembly language, etc. Processor executes an instruction, meaning that it performs/controls the operations called for by that instruction. Processor operably couples with the input interface, with the output interface, with the computer-readable medium, and with

the communication interface to receive, to send, and to process information. Processor may retrieve a set of instructions from a permanent memory device and copy the instructions in an executable form to a temporary memory device that is generally some form of RAM.

(32) The application performs operations associated with controlling other components of the system. Some of these operations may include receiving and/or processing data, e.g., from a pressure gauge(s), a temperature sensor(s), a flow controller(s) being used during pyrolysis or user-inputted data, e.g., a selected linear gas velocity. Other of these operations may include calculating a linear gas velocity based on the data, and/or controlling components of the system (e.g., adjusting feed gas flow rate, reactor temperature, reactor pressure, combinations thereof) based on the received or processed data, or both. This may include adjusting one or more of the feed gas flow rate, reactor temperature, reactor pressure in order to maintain a calculated or user-inputted linear gas velocity (so as to ensure no carbon accumulation) during pyrolysis. This may include adjusting one or more of the feed gas flow rate, reactor temperature, reactor pressure in order to maintain no change in pressure at an upstream pressure gauge and no change in pressure at a downstream pressure gauge (so as to ensure no carbon accumulation) during pyrolysis. Some or all of the operations described in the present disclosure may be controlled by instructions embodied in the application. The operations may be implemented using hardware, firmware, software, or any combination of these methods. The application may be implemented in software (comprised of computer-readable and/or computer-executable instructions) stored in the computer-readable medium and accessible by the processor for execution of the instructions that embody the operations of application. The application may be written using one or more programming languages, assembly languages, scripting languages, etc.

(33) It is noted that devices including the processor, the computer-readable medium operably coupled to the processor, the computer-readable medium having computer-readable instructions stored thereon that, when executed by the processor, cause the device to perform any of the operations described above (or various combinations thereof) are encompassed by the disclosure. The computer-readable medium is similarly encompassed.

(34) A block diagram of another illustrative system **500** is shown in FIG. 5. The system **500** may be configured according to any of the disclosed systems, including system **100** of FIG. 1, comprising various components such as a reactor, a source of a liquid metal, a heater, a cooler, a gas delivery system comprising an inlet, an outlet, and a separation assembly. The system **500** further comprises a controller **502** for controlling operations of the system **500** and components thereof. As described above, such a controller **502** may include an input interface **504**, an output interface **506**, a communication interface **508**, a computer-readable medium **510**, a processor **512**, and an application **514**. The controller **502** and its components may each be configured as described above.

EXAMPLE

(35) The following Example is being submitted to further define various species of the present disclosure. This Example is intended to be illustrative only and is not intended to limit the scope of the present disclosure. As used herein, “room temperature” refers to a temperature of from about 20° C. to about 25° C.

(36) This Example demonstrates the concept of carbon product entrainment by high linear velocity of gas flow in a molten zinc bed reactor system. 200 grams of zinc shot (the source of molten zinc) was loaded in an alumina tube reactor (inner diameter 0.75 inch and outer diameter 1.0 inch), which had one end closed. The reactor was mounted inside an electric furnace and the furnace inside temperature was elevated to 1000° C., which converts the zinc shot to molten zinc. Gas (e.g., feed gas comprising methane) was fed to the reactor through an inlet tubing (quartz tubing, inner diameter of 0.16 inch and outer diameter of 0.24 inch) which reached to 0.5 inch above the bottom of the alumina tube reactor. Gas was fed through the inlet tubing at selected gas flow rates (sccm). The flowing gas generated gas bubbles that moved upwardly through the molten zinc bed. An

outlet allowed for gas (e.g., product gas comprising H₂ and carbon) to flow out of the reactor. A back pressure regulator was mounted downstream of the reactor outlet for the reactor pressure elevation. The reactor pressure was elevated and a downstream pressure gauge positioned between the reactor outlet and the back pressure regulator measured 30 psig (which is 44.7 psia). An upstream pressure gauge was positioned near the inlet. Under a selected gas flow rate, readings from both upstream and downstream pressure gauges were taken to monitor for any increases in upstream pressure. An increase in upstream pressure indicates that carbon product has accumulated within the reactor, blocking gas passage through the molten zinc bed.

(37) First, nitrogen (N₂) gas was introduced into the reactor at a flow rate of 70 sccm. As noted above, the reactor downstream pressure gauge measured 30 psig. FIG. 2 shows a plot of the readings from the upstream and downstream pressure gauges in the reactor while flowing the N₂ at 70 sccm. As shown in FIG. 2, there was no change in reactor upstream pressure over a period of about 19 hours. This indicated no gas flow blockage was occurring within the reactor.

(38) Next, a feed gas containing both CH₄ (at 60 sccm) and N₂ (at 10 sccm) was introduced into the molten zinc bed through the inlet tubing. FIG. 3 shows a plot of the readings from the upstream and downstream pressure gauges in the reactor while flowing the feed gas. As shown in FIG. 3, upstream pressure started to rise after 4 hours of time-on-stream, reaching 37 psig after 7 hours time-on-stream before the experiment was stopped. The increase in upstream pressure was due to carbon product accumulating within the reactor and blocking gas passage through the molten zinc. This blockage makes gas passage increasingly difficult and leads to an increase in upstream pressure to maintain the selected gas flow rate of 70 sccm. The linear gas velocity (cm/s) of the reactor was calculated from Equation 1:

$$(39) \quad \frac{F(\text{cm}^3/\text{s})}{A(\text{cm}^2)} * \left(\frac{T_{\text{reactor}}(\text{K})}{P_{\text{reactor}}(\text{psia})} * \frac{P_{\text{standard}}(\text{psia})}{T_{\text{standard}}(\text{K})} \right) \quad (\text{Equation 1})$$

wherein F is the feed gas flow rate in cm³/s (1.17 cm³/s) at standard temperature and pressure, A is the reactor cross-sectional area (2.57 cm², calculated from the inner diameter of the alumina tube subtracting the outer diameter of the inlet tubing), T_{reactor} is the reactor temperature (1273.15 K), P_{reactor} is the reactor pressure (44.7 psia), P_{standard} is standard pressure (14.7 psia), and T_{standard} is standard temperature (273.15 K). Thus, under these conditions, the linear gas velocity of the reactor was about 0.70 cm/s.

(40) Next, a feed gas containing both CH₄ and N₂ was introduced into the reactor through the inlet. In this case, however, the gas flow rate was 70 sccm (60 sccm CH₄ and 10 sccm N₂) while periodically (every two hours) increasing the flow of N₂ through the molten zinc bed to 510 sccm for one hour (total gas flow rate of 570 sccm). This periodic increase in gas flow rate periodically increased the linear gas velocity (calculated from Equation 1) in the reactor (from 0.70 cm/s to 5.67 cm/s). As shown in FIG. 4, during the 14 hours of methane pyrolysis (7 cycles of 2 hours methane pyrolysis), there was no increase in upstream pressure. Carbon product entrainment could also be visually observed from reactor outlet tubing. The results demonstrate that linear gas velocity may be adjusted to prevent the accumulation of carbon within the reactor, including so that no carbon accumulates within the reactor. Although carbon entrainment has been considered in some existing pyrolysis systems, it was unexpected that accumulation of carbon within the reactor could be completely prevented through adjustments of linear gas velocity.

(41) The word “illustrative” is used herein to mean serving as an example, instance, or illustration. Any aspect or design described herein as “illustrative” is not necessarily to be construed as preferred or advantageous over other aspects or designs. Further, for the purposes of this disclosure and unless otherwise specified, “a” or “an” means “one or more.”

(42) If not already included, all numeric values of parameters in the present disclosure are preceded by the term “about” which means approximately. This encompasses those variations inherent to the measurement of the relevant parameter as understood by those of ordinary skill in

the art. This also encompasses the exact value of the disclosed numeric value and values that round to the disclosed numeric value.

(43) The foregoing description of illustrative embodiments of the disclosure has been presented for purposes of illustration and of description. It is not intended to be exhaustive or to limit the disclosure to the precise form disclosed, and modifications and variations are possible in light of the above teachings or may be acquired from practice of the disclosure. The embodiments were chosen and described in order to explain the principles of the disclosure and as practical applications of the disclosure to enable one skilled in the art to utilize the disclosure in various embodiments and with various modifications as suited to the particular use contemplated. It is intended that the scope of the disclosure be defined by the claims appended hereto and their equivalents.

(44) Any directional language used in the present disclosure such as top, bottom, upper, lower, above, below, and the like is not necessarily intended to be limiting, but rather to provide a point of reference to other elements being described.

(45) As used herein, the term “mount” includes join, unite, connect, couple, associate, insert, hang, hold, affix, attach, fasten, bind, paste, secure, bolt, screw, rivet, solder, weld, glue, form over, form in, layer, mold, rest on, rest against, abut, and other like terms. The phrases “mounted on”, “mounted to”, and equivalent phrases indicate any interior or exterior portion of the element referenced. These phrases also encompass direct mounting (in which the referenced elements are in direct contact) and indirect mounting (in which the referenced elements are not in direct contact, but are connected through an intermediate element). The elements may be mounted permanently, removably, or releasably unless specified otherwise.

Claims

1. A system for hydrocarbon pyrolysis, the system comprising: a reactor configured to contain a liquid metal within an interior chamber of the reactor; a heater operably coupled to the reactor to form a heating zone within a first portion of the interior chamber comprising the liquid metal; a cooler operably coupled to the reactor to form a cooling zone within a second portion of the interior chamber above the first portion; a gas delivery assembly comprising an inlet in fluid communication with the interior chamber, the gas delivery assembly configured to deliver a feed gas comprising a hydrocarbon as a plurality of bubbles through the liquid metal; an outlet in fluid communication with the interior chamber and configured to deliver a product gas to a separation assembly, the product gas formed from pyrolysis of the hydrocarbon in the liquid metal, the product gas comprising H₂ and carbon; and the separation assembly in fluid communication with the interior chamber via the outlet, the separation assembly configured to separate the carbon from other components of the product gas, wherein the reactor is configured to entrain the carbon from pyrolysis of the hydrocarbon in the liquid metal into the product gas without accumulating the carbon in the interior chamber during pyrolysis; wherein the system comprises an upstream pressure gauge configured to measure a pressure of the feed gas during pyrolysis and a downstream pressure gauge configured to measure a pressure of the product gas during pyrolysis, and a controller comprising a processor and a non-transitory computer-readable medium operably coupled to the processor, the non-transitory computer-readable medium comprising instructions, that, when executed by the processor, cause the system to adjust one or more of a feed gas flow rate, a reactor temperature, and a reactor pressure to achieve no change in the pressure of the feed gas during pyrolysis and no change in the pressure of the product gas during pyrolysis.
2. The system of claim 1, further comprising a first recirculation path configured to return separated liquid metal from the separator assembly to the reactor.
3. The system of claim 1, wherein the reactor is configured to achieve a linear gas velocity of at least about 5 cm/s through the interior chamber at a feed gas flow rate of about 300 sccm or higher,

a reactor temperature of about 1000° C., and a reactor pressure of about 147 psia.

4. The system of claim 1, wherein the system does not comprise any other outlet through which carbon exits the interior chamber other than the outlet configured to deliver the product gas to the separation assembly.

5. The system of claim 1, further comprising a controller comprising a processor and a non-transitory computer-readable medium operably coupled to the processor, the non-transitory computer-readable medium comprising instructions, that, when executed by the processor, cause the system to adjust one or more of a feed gas flow rate, a reactor temperature, and a reactor pressure to achieve a linear gas velocity of at least about 5 cm/s through the interior chamber.

6. The system of claim 1, wherein the system further comprises a carrier gas inlet in fluid communication with the interior chamber and configured to deliver a carrier gas to the cooling zone.

7. The system of claim 1, wherein the system does not comprise any other inlet through which a gas enters the reactor other than the inlet of the gas assembly.

8. The system of claim 1, further comprising a source of the liquid metal and the liquid metal consists of zinc.

9. The system of claim 1, further comprising a source of the feed gas.

10. The system of claim 9, wherein the feed gas comprises methane.

11. A system for hydrocarbon pyrolysis, the system comprising: a reactor configured to contain a liquid metal within an interior chamber of the reactor; a heater operably coupled to the reactor to form a heating zone within a first portion of the interior chamber comprising the liquid metal; a cooler operably coupled to the reactor to form a cooling zone within a second portion of the interior chamber above the first portion; a gas delivery assembly comprising an inlet in fluid communication with the interior chamber, the gas delivery assembly configured to deliver a feed gas comprising a hydrocarbon as a plurality of bubbles through the liquid metal; an outlet in fluid communication with the interior chamber and configured to deliver a product gas to a separation assembly, the product gas formed from pyrolysis of the hydrocarbon in the liquid metal, the product gas comprising H₂ and carbon; and the separation assembly in fluid communication with the interior chamber via the outlet, the separation assembly configured to separate the carbon from other components of the product gas, wherein the system does not comprise any other outlet through which carbon exits the interior chamber other than the outlet configured to deliver the product gas to the separation assembly; wherein the system comprises an upstream pressure gauge configured to measure a pressure of the feed gas during pyrolysis and a downstream pressure gauge configured to measure a pressure of the product gas during pyrolysis and the system further comprises a controller comprising a processor and a non-transitory computer-readable medium operably coupled to the processor, the non-transitory computer-readable medium comprising instructions, that, when executed by the processor, cause the system to adjust one or more of a feed gas flow rate, a reactor temperature, and a reactor pressure to achieve no change in the pressure of the feed gas during pyrolysis and no change in the pressure of the product gas during pyrolysis.

12. The system of claim 11, wherein the reactor is configured to achieve a linear gas velocity of at least about 5 cm/s through the interior chamber at a feed gas flow rate of about 300 sccm or higher, a reactor temperature of about 1000° C., and a reactor pressure of about 147 psia.

13. The system of claim 11, further comprising a controller comprising a processor and a non-transitory computer-readable medium operably coupled to the processor, the non-transitory computer-readable medium comprising instructions, that, when executed by the processor, cause the system to adjust one or more of a feed gas flow rate, a reactor temperature, and a reactor pressure to achieve a linear gas velocity of at least about 5 cm/s through the interior chamber.
