

HYDROCARBON PYROLYSIS SYSTEM AND METHOD THEREOF

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority to the Singapore application no. 10202403196P filed 14 October, 2024, the contents of which are hereby incorporated by reference in their entirety for all purposes.

TECHNICAL FIELD

[0002] This application relates generally to the field of hydrocarbon pyrolysis, and more particularly, to a hydrocarbon pyrolysis system and a hydrocarbon pyrolysis method.

BACKGROUND

[0003] Hydrocarbon pyrolysis is a CO_x-free process in which pure hydrogen and solid carbon are produced without producing undesirable greenhouse gas, such as CO₂, due to the absence of an oxidation source. Conventional pyrolysis systems or processes typically achieve reasonable hydrocarbon conversion to hydrogen at elevated high temperatures, for example, above 1200°C without a catalyst or above 800°C with a catalyst. However, such high temperature necessitates the consumption of large amounts of energy, which inevitably results in a high carbon footprint.

SUMMARY

[0004] According to an aspect, disclosed herein is a hydrocarbon pyrolysis system. The hydrocarbon pyrolysis system comprises a reactor defining an interior chamber, an operating temperature in the interior chamber being controllable; and at least one catalytic membrane disposed in the interior chamber, wherein each of the at least one catalytic membrane comprises

a support layer disposed between a catalytic layer and a hydrogen purifying layer, wherein the catalytic layer is configured to react with a hydrocarbon to form hydrogen and carbon nanotubes simultaneously during hydrocarbon pyrolysis, wherein the hydrogen purifying layer is configured to selectively remove hydrogen from the interior chamber during hydrocarbon pyrolysis.

[0005] According to another aspect, disclosed herein is a hydrocarbon pyrolysis method. The method comprises maintaining a hydrocarbon in an interior chamber at an operating temperature to form hydrogen and carbon nanotubes simultaneously; depositing the carbon nanotubes on a catalytic layer of at least one catalytic membrane, wherein each of the at least one catalytic membrane comprises a support layer disposed between the catalytic layer and a hydrogen purifying layer; and concurrent to depositing the carbon nanotubes, selectively removing the hydrogen from the interior chamber with the at least one catalytic membrane, wherein the at least one catalytic membrane is carbon nanotube impermeable.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] Various embodiments of the present disclosure are described below with reference to the following drawings:

[0007] FIG. 1 is a schematic diagram of a hydrocarbon pyrolysis system according to embodiments of the present disclosure.

[0008] FIG. 2 is a schematic side view of a catalytic membrane in a disc structure according to embodiments of the present disclosure.

[0009] FIG. 3 is a schematic front view of a catalytic membrane in a tubular structure according to embodiments of the present disclosure.

[0010] FIGs. 4A and 4B are schematic diagrams of a hydrocarbon pyrolysis system during operation according to embodiments of the present disclosure.

[0011] FIG. 5 is a flow chart illustrating a hydrocarbon pyrolysis method.

[0012] FIG. 6 is a schematic diagram illustrating simultaneous hydrogen and carbon nanotubes production via hydrocarbon pyrolysis process of an exemplary implementation.

[0013] FIG. 7 shows the change in the methane conversion with H₂ recovery with varying reactor temperature at ambient pressure for the exemplary implementation.

[0014] FIG. 8A and 8B are blueprints of the exemplary implementation.

[0015] FIG. 9A shows a relationship between methane conversion and temperature for an exemplary methane pyrolysis activity of the exemplary implementation.

[0016] FIG. 9B shows a stability study between methane conversion and H₂ flux for a conventional system.

[0017] FIG. 9C shows a relationship between H₂ recovery and H₂ selectivity for a conventional system.

[0018] FIG. 10A shows carbon nanotube recovery using a solvent-assisted method.

[0019] FIG. 10B shows carbon nanotube recovery using a fluidization method.

[0020] FIG. 11 shows CO₂ oxidizing carbon residue to produce CO for the exemplary implementation.

DETAILED DESCRIPTION

[0021] The following detailed description is made with reference to the accompanying drawings, showing details and embodiments of the present disclosure for the purposes of illustration. Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments, even if not explicitly described in these other embodiments. Additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0022] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0023] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance as generally understood in the relevant technical field, e.g., within 10% of the specified value.

[0024] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0025] As used herein, terms “concurrently”, “simultaneously”, “at the same time”, or the like, may refer to events or actions that coincide or overlap within a period of time, regardless of whether the events start at the same time instant, and regardless of whether the events end at the same time instant.

[0026] Conventional hydrocarbon pyrolysis processes often involve high temperatures such as above 1200°C without a catalyst or above 800°C with a catalyst. However, such high temperature necessitates the consumption of large amounts of energy, which inevitably results in a high carbon footprint.

[0027] The present disclosure discloses a proposed hydrocarbon pyrolysis system which comprises an integrated catalytic membrane configuration. Addressing the various limitations, the proposed hydrocarbon pyrolysis system and method may be operated at a lower operating temperature (for example, below 800°C) in comparison to conventional processes, while still achieving high hydrogen (H₂) yield. The catalytic membrane comprises catalytic sites acting as sites/surfaces for carbon (or carbon nanotube) formation or growth. In addition, the catalytic membrane comprises a hydrogen purifying layer. With the hydrogen purifying layer, H₂ produced during the catalytic reaction is selectively removed/separated from the hydrocarbons and hydrogen product mixture simultaneously, thereby overcoming the thermodynamic

equilibrium conversion limitation of hydrocarbon pyrolysis. Carbon-related products, such as carbon nanotubes, may be concurrently produced in the hydrocarbon pyrolysis process.

[0028] In addition, a carbon-negative hydrocarbon pyrolysis method may be achieved with the proposed hydrocarbon pyrolysis system. CO_x compounds, such as carbon dioxide, may be used as an oxidant compound for regenerating the catalytic membrane. As the catalytic sites bond strongly with the catalytic membrane, carbon residues (such as residual carbon nanotubes) which are unrecovered and/or left on the catalytic membrane may be gasified by the oxidant compound at similar operating temperatures (such as between 550°C to 650°C), thus resulting in minimal or no loss of catalytic sites or catalytic surfaces for subsequent hydrocarbon pyrolysis process. This presents a novel and efficient regenerative catalytic membrane for hydrocarbon pyrolysis.

[0029] The proposed hydrocarbon pyrolysis system presents an integrated solution for facile carbon product recovery during H₂ production from hydrocarbon pyrolysis, such as methane pyrolysis. This is enabled by a valve bypass for carbon recovery, which allows catalyst regeneration, enabling pseudo-continuous H₂ production. Departing from conventional methods, the proposed system enables simultaneous removal of ultra-pure H₂ from the hydrocarbon pyrolysis product mixture in overcoming the thermodynamic limitations, while concurrently enabling high H₂ yields at a relatively lower operating temperature. In various embodiments, highly valued metal-free (or low metal content) carbon nanotube or carbon nanofiber growth may be produced. In addition, single-wall / multi-wall carbon nanotubes may also be produced. The nature of the carbon nanotubes formed may be altered or varied based on various requirements by changing the size and metal-to-support interactions at the outer layer of the catalytic membrane process. The proposed hydrocarbon pyrolysis system and method enable zero CO₂ or even negative CO₂ emissions, as CO₂ may be used as a mild oxidant

for the regeneration of the catalyst at operating temperature or reaction temperature, thus providing an overall process with net negative CO₂ emissions.

[0030] According to one aspect, FIGs. 1 and 2 illustrate schematically a hydrocarbon pyrolysis system 50 according to various embodiments of the present disclosure. The hydrocarbon pyrolysis system 50 may comprise a reactor 100 defining an interior chamber 110. The interior chamber 110 may have an operating temperature which is controllable. In some embodiments, the reactor 100 may comprise a temperature sensor controller for controlling or maintaining the operating temperature in the interior chamber at a temperature range of up to 800°C.

[0031] The reactor 110 may further include at least one catalytic membrane 200 disposed in the interior chamber 110. For ease of elaboration and clarity, the embodiment as described herein and illustrated in FIG. 1, comprises a single catalytic membrane 200. It may be appreciated that various embodiments of the disclosure may comprise multiple catalytic membranes 200.

[0032] In various embodiments, the reactor 100 may comprise an inlet 120. The inlet 120 may be in fluid communication with the interior chamber 110. The inlet 120 may be in fluid communication with a hydrocarbon source 300 and an oxidant source 400 via respective valves 310/410. By independently controlling each of the valves 310/410, the inlet 120 may be in a selectable fluid communication with the hydrocarbon source 300 and the oxidant source 400. In other words, at each time instance, the inlet 210 may be in fluid communication with the hydrocarbon source 300 or the oxidant source 400. However, the inlet 210 may not be in fluid communication with both the hydrocarbon source 300 and the oxidant source 400 at a single time instance. The hydrocarbon source 300 may hold or contain a hydrocarbon such as methane, ethane, propane or heavy hydrocarbons such as waste-derived tars. The oxidant source may hold or contain a mild oxidant, such as CO₂ or NO_x.

[0033] In various embodiments, the reactor 100 may further comprise an outlet 130. The outlet 130 may be in fluid communication with the interior chamber 110. The outlet 130 may be in fluid communication with a carbon collection system 500 via a valve 510. Hence, the carbon collection system 500 may be in fluid communication with the interior chamber 110. The carbon collection system 500 may be configured for collecting carbon-related products from the reactor 100. The carbon collection system 500 may be a carbon nanotube collection system 500. The carbon nanotube collection system 500 may comprise a gas-solid separator 520 for separating a gaseous carbon product from a solid carbon product from the reactor 100. The gas-solid separator 520 may be connected with a gas outlet pipe and a solid collector. The solid collector may comprise one or more quartz containers.

[0034] In various embodiments, the reactor 100 may further comprise a hydrogen discharging port 140. The hydrogen discharging port 140 may be in fluid communication with a hydrogen discharging system 600. Hence, the hydrogen discharging system 600 may be in fluid communication with the interior chamber 110. The hydrogen discharging system may comprise a hydrogen membrane and a gas pipeline. The hydrogen membrane may be in the form of a thin ceramic film layer, such as a palladium film. The thickness of the palladium film is ~10 micron.

[0035] In various embodiments, the catalytic membrane 200 may separate the interior chamber 110 into a first sub-chamber 112 and a second sub-chamber 114. The first sub-chamber 112 of the interior chamber 110 may be in fluid communication with the inlet 120 and the outlet 130. The second sub-chamber 114 may be in fluid communication with the hydrogen discharging port 140.

[0036] Further referring to FIG. 2, in various embodiments, the catalytic membrane 200 may be configured in a disc structure. The catalytic membrane 200 may comprise a support layer 210 disposed between a catalytic layer 220 and a hydrogen purifying layer 230. The catalytic

layer 220 is thus separated from the hydrogen purifying layer 230 by the supporting layer 210. In various embodiments, the catalytic layer 220 may be facing the first sub-chamber 112 and the hydrogen purifying layer 230 may be facing the second sub-chamber 114. The catalytic layer 220 of the catalytic membrane 200 may be configured to react with a hydrocarbon to form hydrogen and carbon nanotubes simultaneously during hydrocarbon pyrolysis. In addition, the hydrogen purifying layer 230 may be configured to separate hydrogen from a mixture of hydrocarbon and the carbon nanotubes formed during hydrocarbon pyrolysis, to selectively remove hydrogen from the interior chamber 110. As such, the catalytic membrane 200 may be configured to selectively remove hydrogen from the interior chamber 110. In various embodiments, with the provision of the hydrogen purifying layer 230, in addition to providing a catalytic function, the catalytic membrane 200 may concurrently act as a H₂ purifier (or perform H₂ purification process). This enables high-purity H₂ to be collected at the hydrogen discharging system 600, thus alleviating the need for additional downstream H₂ purification.

[0037] In various embodiments, the catalytic membrane 200 may be carbon nanotube impermeable. In other words, the catalytic membrane 200 does not allow carbon nanotube to permeate through it, and thus allows the carbon nanotubes formed during hydrocarbon pyrolysis to be captured or formed on the catalytic membrane 200. In various embodiments, at least the support layer 210 of the catalytic membrane 200 is carbon nanotube impermeable. Hence, the carbon nanotube formed during hydrocarbon pyrolysis is captured or formed on the support layer 210. In an example, the support layer is an Al₂O₃ layer. In other examples, the support layer may be a stainless steel layer, a MgO layer or a SiO₂ layer. In other examples, the support layer may comprise at least one of or a combination of: Al₂O₃, stainless steel, MgO and SiO₂.

[0038] In various embodiments, the catalytic layer 220 may comprise a metal-based alumina-silicate layer or a metal-based perovskite layer. The catalytic layer 220 may comprise active metal(s) catalysts decorated on the surface of the support layer 210. In various embodiments,

the catalytic layer 220 may comprise at least one of: Nickel, Iron, Copper, Zinc, Cobalt, and rare earth metals, including but not limited to: CeO_2 and La_2O_3 . The catalytic layer 220 is not limited to a layer formed on the catalytic membrane 200, but may instead be functionalized on fluidizing beads/particles comprising and not limited to Al_2O_3 material. In various embodiments, the catalytic layer 220 may comprise a functionalized surface on the support layer 210. The functionalized surface may comprise fluidizing particles on the support layer 210. In other embodiments, the catalytic layer 220 may include core-shell architectures, embedded configurations, or hierarchical supports such as zeolites.

[0039] In various embodiments, the hydrogen purifying layer may be a Pd layer, a Pd-alloy layer or a perovskite-based layer. In other embodiments, the hydrogen purifying layer may be a Ni Layer, a Ni-alloy layer, a Pd-Ni-alloy layer.

[0040] Further referring to FIG. 3, in various embodiments, the catalytic membrane 200 may be configured in a tubular structure. In an example, the catalytic membrane 200 is a hollow fibre membrane. The catalytic membrane 200 may comprise an annular structure, with a support layer 210 disposed between a catalytic layer 220 and a hydrogen purifying layer 230. The catalytic layer 220 is thus separated from the hydrogen purifying layer 230 by the supporting layer 210. The catalytic layer 220 may be an inner layer facing the first sub-chamber 112, and the hydrogen purifying layer 230 may be an outer layer facing the second sub-chamber 114.

[0041] It may be appreciated that the catalytic membrane 200 may be configured in various other shapes (hollow fiber, tubular, disc).

[0042] In an example, the catalytic membrane 200 may comprise two layers formed on opposing sides of the hollow fiber or tubular ceramic support. The outer layer (catalytic layer 220) of $\sim 5\text{-}10\ \mu\text{m}$ thickness may include metal-based alumina-silicate layer for hydrocarbon pyrolysis reactions. Metals can include Ni, Fe, Cu, Zn, etc. The inner layer (hydrogen purifying layer 230) of Pd-alloy of $1\text{-}5\ \mu\text{m}$ thickness for continuous ultra-pure H_2 separation.

[0043] The proposed hydrocarbon pyrolysis system 50 may be a two-stage hydrocarbon pyrolysis system 50, with a first stage corresponding to the production of H₂ as well as carbon related products (such as carbon nanotubes) on a catalytic surface, and a second stage corresponding to a regeneration of the catalytic surface for a continuous hydrocarbon pyrolysis process.

[0044] FIGs. 4A and 4B illustrate an operation of the hydrocarbon pyrolysis system 50. FIG. 4A illustrates a first stage 50A of a hydrocarbon pyrolysis method corresponding to the production of H₂ and carbon-related products (such as carbon nanotubes) on a catalytic surface, as well as the recovery of carbon-related products. In the first stage 50A, the operating temperature of the interior chamber 110 may be maintained or controlled at a temperature range of between 400°C to 800°C for hydrocarbon pyrolysis. It is worth noting that the temperature range is lower than typical conventional hydrocarbon pyrolysis systems. Hydrocarbon (HC), such as methane, may be provided from the hydrocarbon source 300 to the interior chamber 110 via valve 310 with valve 410 remaining closed. In some embodiments, the hydrocarbon is provided to the first sub-chamber 112 of the reactor 100.

[0045] With the catalytic layer 210 of the catalytic membrane 200 catalyzing the hydrocarbon pyrolysis reaction at the operating temperature of the interior chamber 110, the hydrocarbon undergoes pyrolysis to form H₂ and carbon-related products (C), such as carbon nanotubes or carbon nanofibres. As previously described, the catalytic member 200 is hydrogen permeable and hence allows selective removal of the H₂ formed during the hydrocarbon pyrolysis reaction. Simultaneously or concurrently with the production of H₂ and carbon nanotubes, some or most of the H₂ formed during the hydrocarbon pyrolysis reaction may be selectively removed from the interior chamber 110 via the catalytic membrane 200. The selective removal of H₂ may be driven by a pressure differential between the interior chamber 110 and the exterior of the reactor 100. In some embodiments, the H₂ formed in the first sub-chamber 112 may be selectively

moved to the second sub-chamber 114 through the catalytic membrane 200. This may be driven by a pressure differential across the catalytic membrane 200 between the first sub-chamber 112 and the second sub-chamber 114. In some embodiments, the H₂ formed in the first sub-chamber 112 may be selectively moved to the second sub-chamber 114 through the catalytic membrane 200 by a H₂ partial pressure difference across the catalytic membrane 200 between the first sub-chamber 112 and the second sub-chamber 114. The catalytic membrane 200 enables high-purity H₂ to be produced and discharged from the interior chamber 110 via the hydrogen discharging port 140, and eventually captured by the hydrogen discharging system 600.

[0046] The selective removal of H₂ during the hydrocarbon pyrolysis reaction overcomes the thermodynamic equilibrium conversion limitation of hydrocarbon pyrolysis, and thus allowing a continuous hydrocarbon pyrolysis process with high yield of H₂. In addition, the carbon nanotubes (C) may be deposited on or formed on the catalytic layer 220. The carbon nanotubes may be recovered or collected from the interior chamber 110 via solvent-assisted methods or gas-phase fluidization methods.

[0047] FIG. 4B illustrates a second stage 50B of a hydrocarbon pyrolysis method corresponding to the regeneration of the catalytic surface 220. While carbon nanotubes deposited on or attached to the catalytic layer 220 may be recovered using the above-described solvent-assisted or fluidization methods, residual carbon nanotubes may remain on the catalytic layer 220 after recovery, which inevitably reduces the catalytic effect of the catalytic layer 220 due to a reduction in catalytic surface or catalytic sites. The catalytic life of the catalytic membrane 200 may be enhanced by a regeneration process.

[0048] In various embodiments, the catalytic layer 220 may be regenerable with a mild oxidant from the oxidant source 400. The residual carbon on the catalytic layer 220 may be removed to regenerate the catalytic layer 220. During the catalytic regeneration process of the catalytic surface 220, the valve 310 may be closed and valve 410 may be opened to provide the

mild oxidant to the interior chamber 220. As non-limiting examples, the mild oxidant may include CO₂, air, or NO_x.

[0049] The mild oxidant may be provided to the interior chamber 220 to react with the residual carbon on the catalytic layer 220 at the operating temperature. In exemplary embodiments, CO₂ may be provided to the interior chamber 220 to react with the residual carbon on the catalytic layer 220 to form Carbon Monoxide (CO) at the operating temperature. Advantageously, the first stage 50A of hydrogen and carbon nanotube production may be operated at the same operating temperature as the second stage 50B of carbon nanotube recovery and catalytic layer regeneration. This enables a continuous hydrocarbon pyrolysis process in which the production and recovery of products may be operated seamlessly without requiring material changes in operating temperature. In addition, carbon recovery may also aid in the regeneration of the catalytic layer 220, thus renewing the catalytic efficiency of the catalytic layer.

[0050] During the carbon nanotube recovery process and/or the catalytic regeneration process, valve 510 may be opened such that the carbon collection system 500 is in fluid communication with the interior chamber 110 via the outlet 130. The carbon collection system 500 may be configured for collecting carbon-related products from the reactor 100 as well as the CO produced during catalytic regeneration. The gas-solid separator 520 may be used for separating a gaseous carbon product, such as the CO, from a solid carbon product, such as the carbon nanotubes.

[0051] In various embodiments, a bonding force between the support layer 210 and the catalytic layer 220 is stronger than an attachment force between the carbon nanotubes and the catalytic layer 220. This enables the carbon nanotubes to be effectively removed from the catalytic layer 220 with minimal material loss to the catalytic layer 220. This aids in preserving the catalytic efficiency of the catalytic layer 220.

[0052] According to another aspect of the present disclosure, a hydrocarbon pyrolysis method 700 is disclosed. Referring to FIG. 5, in various embodiments, the hydrocarbon pyrolysis method 700 comprises: in 710, maintaining a hydrocarbon in an interior chamber at an operating temperature to form hydrogen and carbon nanotubes simultaneously via pyrolysis; in 720, depositing the carbon nanotubes on a catalytic layer of at least one catalytic membrane, wherein each of the at least one catalytic membrane comprises a support layer disposed between the catalytic layer and a hydrogen purifying layer; and in 730, concurrent to depositing the carbon nanotubes, selectively removing the hydrogen from the interior chamber with the at least one catalytic membrane, wherein the at least one catalytic membrane is carbon nanotube impermeable.

[0053] In various embodiments, the hydrocarbon pyrolysis method further comprises recovering the carbon nanotubes using at least one of: a solvent-assisted method and a gas-phase fluidization method. In various embodiments, the hydrocarbon pyrolysis method further comprises regenerating the catalytic layer by oxidizing carbon nanotubes on the catalytic layer with a mild oxidant at the operating temperature. In various embodiments, the mild oxidant comprises at least one of: CO₂ and NO_x. In various embodiments, the mild oxidant has a concentration in a range of 5 to 100%. In various embodiments, the hydrocarbon comprises at least one of: methane, ethane, propane and waste derived tars.

[0054] In various embodiments, the hydrocarbon pyrolysis method further comprises maintaining the operating temperature at a temperature range of between 400°C to 800°C. In various embodiments, the temperature range is between 500°C to 650°C. In various embodiments, the interior chamber is at a pressure of 0.55MPa.

[0055] In an exemplary embodiment, disclosed herein is a catalytic membrane process for hydrocarbon pyrolysis. The catalytic membrane process is in two stages, namely, (i) pyrolysis of hydrocarbons to generate solid metal-free carbon nanotubes and H₂, (ii) regeneration of

deactivated catalytic sites with mild oxidant (i.e, CO₂). A proposed hydrocarbon pyrolysis system converts lighter and heavy hydrocarbons into H₂ gas with carbon nanotubes at a significantly lower temperature than conventional processes, while maintaining a high H₂ production yield. The catalytic membrane process in the hydrocarbon pyrolysis system comprises the following steps: (1) hydrocarbons in vapor state enter a reactor containing H₂-permeable membrane(s), with active metals catalysts decorated on the surface or around the membrane(s), catalyzing hydrocarbon pyrolysis reaction to H₂ and carbon nanotubes; (2) H₂ produced is selectively removed simultaneously from the hydrocarbons and hydrogen product mixture into the membrane(s) during the catalytic reaction, thereby overcoming the thermodynamic equilibrium conversion limitation of hydrocarbon pyrolysis; (3) Carbon nanotubes (CNTs) grown on active metal centers without dislodging the metals interacting with the support can be recovered by fluidization or solvent-assisted treatment, and/or gasified with CO₂ to form CO.

[0056] **Exemplary Implementation**

[0057] This section discloses an exemplary implementation of the proposed hydrocarbon pyrolysis system and hydrocarbon pyrolysis method. FIG. 6 illustrates a 2-stage catalytic membrane process for the production of ultra-pure hydrogen and high-quality Carbon nanotubes (CNTs) from hydrocarbon pyrolysis reaction. As the hydrocarbon decomposition reaction is an endothermic and equilibrium-driven reaction, high H₂ yields are often achievable only at high reaction temperatures, such as above 800°C. The proposed system and method present the use of a catalytic membrane in the hydrocarbon pyrolysis process with the simultaneous removal of H₂ produced, to obtain high H₂ yields at a relatively lower temperature. In the first stage, the membrane reactor comprises an active catalytic layer and a metal-based H₂ membrane for selectively removing H₂ from the reaction mixture, thereby driving the chemical reaction equilibrium forward.

[0058] The combination of catalyst and membrane produces a synergetic effect on the overall performance for hydrocarbon pyrolysis reaction in an integrated catalytic membrane reactor. Using methane as an example of a typical hydrocarbon, FIG. 7 shows the calculated methane conversion results in an integrated catalytic membrane reactor with and without H₂ recovery from the membrane module at ambient pressures. Referring to FIG. 7, at all the reaction temperatures, a significant enhancement in methane conversion was observed with simultaneous H₂ recovery. It may be seen that the methane conversion was also influenced by the amount of H₂ recovered. For example, a near 100% of CH₄ conversion is achieved at 700°C with 80% of H₂ recovery in the proposed process. At the same temperature, a setup without the catalytic membrane is only able to achieve less than 80% of methane conversion. Further, at 550°C and ambient pressure, the single-pass methane conversion may be achieved up to 77% with a H₂ recovery of 80% in the proposed process. To achieve a result similar to single-pass methane conversion, a temperature of about 700 °C is required for a setup without the catalytic membrane, which is about 150 °C of higher temperature. This is accompanied with the requirement of a downstream H₂ purification process to recover high-purity H₂. The integrating of the H₂ permeable membrane with a catalytic layer for methane pyrolysis catalyst enables high single-pass methane conversions at milder operating conditions (such as lower operating temperature and pressure), concurrently alleviating downstream H₂ purification process.

[0059] FIGs. 8A and 8B show a blueprint of a prototype of a hydrocarbon pyrolysis system with an integrated catalytic membrane. The prototype has the following specifications: (1) Design temperature: 800 °C; design pressure: 0.55 MPa. (2) Working pressure: the normal pressure is ~0.55MPa. Gases including methane, hydrogen, argon and nitrogen can be fed into the reaction chamber. (3) Product dimensions: 900 mm length, 440 mm width, 2,020 mm height. (4) Reaction system parameters: The heating zone of the furnace is 600 mm long, with an insulation area of about 300 mm. The theoretical maximum heating temperature of the

heating system is 1000 °C and is equipped with a temperature sensor controller. The reaction chamber is interchangeable between two different materials of either quartz or stainless steel. The inner diameter of the reaction tube (DN 40) is ~40 mm and the length is ~970 mm; the discharge pressure of the safety valve is 0.55 MPa. (5) Carbon nanotube collection and separation system: The gas-solid separator is composed of a quartz tube with an inner diameter of 100 mm, a wall thickness of ~3.5 mm and a total length of ~930 mm. It adopts a two-stage design, and the top of the gas-solid separator is connected with a gas outlet pipe with an inner diameter of 8 mm. The solid collector is composed of quartz containers with an outer diameter of ~200 mm, a wall thickness of ~3.5 mm and a total length of ~445 mm. The inner diameter of the pipe connecting the solid collector and the gas-solid separator is ~50 mm. (6) Hydrogen discharge system: the hydrogen discharging system is composed of a hydrogen membrane and a gas pipeline. The hydrogen membrane is composed of a ceramic thin film layer with an outer diameter of 12 mm, an inner diameter of 8mm and a length of 350 mm. The thickness of the palladium film is ~10 micron, and the gas pipeline is composed of a stainless steel pipe and pipe fittings with an outer diameter of 8 mm. At a pressure of 1 kg, the pure hydrogen flow rate is about 2 L/min.

[0060] **Materials and Methods**

[0061] Thermodynamic analysis for the proposed integrated membrane reactor

[0062] Thermodynamic equilibrium of methane pyrolysis at any given temperature and pressure is calculated by minimization of Gibbs free energy of a multicomponent system. The total Gibbs free energy is the summation of all chemical potential of the species that can be found in methane pyrolysis reaction (i.e., methane, solid carbon, hydrogen). Pressure at 1 bar is chosen to calculate the chemical potentials since low pressure favors higher conversion of methane in methane pyrolysis governed by Le Chatelier's principle. The simulation assumes pure CH₄ is used for pyrolysis reaction. Peng-Robinson Equation of State is chosen to estimate

the fugacity coefficient estimations for non-polar systems. Thermodynamic equilibrium calculations were performed on Aspen Plus V10 using RGibbs reactor. Thermodynamic limits at a particular temperature and pressure can be overcome by constantly removing products in the reaction mixture. Le Chatelier's principle suggests that in doing so, thermodynamic conversion will increase. Fundamentally, the equilibrium constant remains unchanged at the same temperature. Hence, it can be exploited to calculate the new equilibrium conversion in an integrated membrane reactor design at varying hydrogen recoveries.

[0063] Catalytic Membrane Reactor

[0064] The catalytic membrane reactor can be either disk shape or tubular shape as shown in FIGs. 2 and 3. For the fabrication of the catalytic membrane reactor, the central Al_2O_3 like substrate acts as a support to synthesize both the catalyst layer and the Pd-alloy layer on opposing sides. The α -alumina support substrate used in the current implementation was synthesized by phase inversion method. Prior to the usage, the calcined substrate was washed with 1M nitric acid (HNO_3) for 4 hours followed by washing in deionized (DI) water.

[0065] For the synthesis of the catalyst layer, firstly, a silica-rich zeolite layer was coated using the secondary growth method, where the outer layer was seeded with zeolite seeds, and then the layer was grown under hydrothermal treatment. For instance, LTA-zeolite was coated on the outer surface of Al_2O_3 substrate. The zeolite membrane/seeds was/were deposited using a synthesis solution in a molar ratio of 50 Na_2O :1 Al_2O_3 :5 H_2O :1000 H_2O . In this process 22.22 gm of NaOH was added to 100 ml of water followed by dissolving 1.147g of sodium aluminate (NaAlO_2) and the solution was stirred for 30 min for complete dissolution. 4.825 ml of sodium silicate solution was added dropwise to the aluminate solution under vigorously stirring condition. The solution was stirred for 4 hours to form a transparent gel. For the seed preparation, the gel was put inside a Teflon liner inside a stainless-steel autoclave and hydrothermal treatment was carried out for 24 hours at 60°C. The formed LTA zeolite was

collected by centrifuge method, and particle size above 200 μm size was sieved out. The zeolite particles of $\leq 200 \mu\text{m}$ size were used as seeds. The cleaned substrate was seeded by dip coating method using 10 wt.% zeolite water suspension. The process was repeated for 4-5 times with intermediate drying at 100 C for 1 hour. Finally, the seeded substrate was put inside an autoclave containing freshly prepared gel of similar composition as mentioned previously and treated under hydrothermal at 60°C for 24 hours. The membrane was taken out and cleaned thoroughly in deionized water several times to remove the unreacted base or silica residue. The membrane was finally dried overnight at 100°C. After depositing the zeolite-like layer, the membrane was placed into a Teflon-lined autoclave, which comprises aqueous Ni precursor and urea solution. The concentration of Ni in the solution is about 10wt% and molar ratio of Ni:urea is 1:10. The autoclave is placed at 180°C for 4h. After the hydrothermal treatment, the membrane is thoroughly washed with DI water and dried in an oven at 100°C for 24hrs, subsequently calcined at 500°C for 5hrs.

[0066] After the catalyst layer growth on one side of the alumina support, the other side is subjected to the growth of either Pd or Pd-alloy layer. The Pd or Pd-alloy layer on one side of the alumina substrate is deposited using electroless deposition method. For instance, to coat with Pd layer, firstly, the substrate was seeded by two-step sensitization/ activation process using acidic solution of SnCl_2 (3.7 g/L) and PdCl_2 (0.88 g/L) solution. During these steps, the catalyst layer was protected using removable Teflon tape. The two-step sensitization/activation process was repeated for 10 times and the substrate was cleaned with DI water followed by oven drying. The activated substrate was further subjected to electroless deposition using hydrazine-based plating baths. The plating solution was prepared by dissolving 0.2 gm of PdCl_2 into 18 ml NH_4OH in 82 ml water under ultrasonic conditions, further, 3.8 gm of Na_2EDTA was added to this and stirred for 30 min until a clear solution appeared. The solution was preheated to 60°C in a water bath and recirculated inside the activated hollow fiber substrate.

Hydrazine was added batch-wise to the plating solution and the pH was also adjusted with time adding drops of NH_4OH . After Pd deposition the membrane was cleaned in DI water until the pH becomes ~ 7 and dried at 100°C overnight.

[0067] After completion of Pd-coating the protected Teflon layer was removed and the obtained catalytic membrane reactor was used for hydrocarbon cracking/pyrolysis process for simultaneous pyrolysis on the catalyst surface and ultra-pure H_2 removal using Pd or Pd-alloy layer.

[0068] **Experiments**

[0069] FIG. 9A shows the results from a preliminary catalytic membrane lab-scale experiment performed for methane pyrolysis reaction at various temperatures and stability at 550°C . The results showed that at 600°C , the methane conversion may be achieved at a higher rate than typical thermodynamic equilibrium conversion and is further accompanied with a H_2 recovery of 70%. In comparison to conventional methods, as shown in FIG. 9B and 9C, a catalyst-coated H_2 permeable membrane reactor only provided a nearly stable single-pass methane conversion of around 40% for a tested period of 35 hrs.

[0070] In the implementation, carbon nanotubes were recovered via either solvent-assisted methods or gas-phase fluidization methods. It was found that solvent-assisted method allows recovery of up to 75% of the carbon with trace amounts of metal present. FIG. 10A (Method 1) shows the SEM images and EDX of Ni edge data before and after recovering the CNTs from the catalytic membrane reactor after solvent-assisted treatment. The result shows that most of the carbon nanotubes were successfully recovered. In addition, the EDX data shows that the recovered carbon nanotubes have negligible traces of Ni metal, with most of the Ni metal species remaining on the catalytic membrane surface.

[0071] Further referring to FIG. 10B (Method 2), gas-phase fluidization method with solid particles fluidized were employed within the catalytic membrane reactor for a short period of

time. It was found that such fluidization method may be used to recover the carbon nanotubes. During fluidization, these solid particles carry the separated carbon nanotubes from the reactor. The SEM images in FIG. 10B shows that the carbon nanotubes may be removed by the fluidization method.

[0072] In stage 2 corresponding to the regeneration process, unrecovered or residual carbon nanotubes were oxidized with a mild oxidant, such as CO₂, to form CO (i.e., reverse Boudouard reaction) at the same operating temperature (i.e., 550°C to 650°C) as the hydrocarbon pyrolysis process. Both the hydrocarbon pyrolysis process and regeneration process may be performed within the integrated catalytic membrane reactor at a common operating temperature. FIG. 11 illustrates the amount of CO₂ reacting with carbon residuals to form carbon monoxide (CO), a useful compound, which may be further utilized to produce more valuable chemicals via the Fischer-Tropsch (FT) reaction.

[0073] The proposed system and method enable the pyrolyzing of hydrocarbons, producing high-purity H₂ and high-quality metal-free carbon nanotubes at relatively lower operating temperatures. In addition, the proposed hydrocarbon pyrolysis process may be a carbon negative process by utilizing CO₂ for the gasification of unrecovered carbon nanotubes to regenerate the catalytic membrane effectively without varying operating processes (i.e., temperature and pressure).

[0074] In various embodiments, proposed herein a catalytic hollow fiber membrane system and process for the use of simultaneous hydrogen separation and carbon nanotubes growth for hydrocarbons pyrolysis applications. Recovery of carbon nanotubes formed during hydrocarbon pyrolysis may be achieved through an inert gas-assisted fluidization process at moderate temperatures and a solvent-assisted process at lower temperatures. In addition, mild oxidants (such as CO₂, air, NO_x, etc) in various concentrations (5 to 100%) may be used for regeneration of the catalytic membrane 200.

[0075] The proposed hydrocarbon pyrolysis system uses hydrocarbons (such as natural gas) to produce pure hydrogen at carbon-neutral or even carbon-negative with the use of mild oxidants (such as CO₂) for catalytic membrane regeneration. This effectively converts CO_x polluting natural gas/ hydrocarbons as a fuel for catalytic membrane regeneration, thus achieving zero-carbon footprint while producing hydrogen fuel economically and productively.

[0076] All examples described herein, whether of apparatus, methods, materials, or products, are presented for the purpose of illustration and to aid understanding, and are not intended to be limiting or exhaustive. Modifications may be made by one of ordinary skill in the art without departing from the scope of the invention as claimed.

CLAIMS

1. A hydrocarbon pyrolysis system, comprising:
 - a reactor defining an interior chamber, an operating temperature in the interior chamber being controllable; and
 - at least one catalytic membrane disposed in the interior chamber, wherein each of the at least one catalytic membrane comprises a support layer disposed between a catalytic layer and a hydrogen purifying layer,
 - wherein the catalytic layer is configured to react with a hydrocarbon to form hydrogen and carbon nanotubes simultaneously during hydrocarbon pyrolysis,
 - wherein the hydrogen purifying layer is configured to selectively remove hydrogen from the interior chamber during hydrocarbon pyrolysis.
2. The hydrocarbon pyrolysis system as recited in claim 1, wherein the at least one catalytic membrane is carbon nanotube impermeable.
3. The hydrocarbon pyrolysis system as recited in any one of above claims, wherein the carbon nanotubes are formed on the catalytic layer during hydrocarbon pyrolysis.
4. The hydrocarbon pyrolysis system as recited in any one of above claims, wherein the catalytic layer is regenerable with a mild oxidant at the temperature.
5. The hydrocarbon pyrolysis system as recited any one of above claims, wherein a bonding force between the support layer and the catalytic layer is stronger than an attachment force between the carbon nanotubes and the catalytic layer.

6. The hydrocarbon pyrolysis system as recited in any one of above claims, wherein the reactor further comprises: an inlet in fluid communication with the interior chamber, the inlet in a selectable fluid communication between a hydrocarbon source and an oxidant source.

7. The hydrocarbon pyrolysis system as recited in any one of above claims, wherein the reactor further comprises: a carbon nanotube collection system in fluid communication with the interior chamber, the carbon nanotube collection system comprising a gas-solid separator.

8. The hydrocarbon pyrolysis system as recited in any one of above claims, wherein the reactor further comprises: a hydrogen discharging system in fluid communication with the interior chamber, the hydrogen discharging system comprising a hydrogen membrane.

9. The hydrocarbon pyrolysis system as recited in any one of above claims, wherein the catalytic layer comprises a metal-based alumina-silicate layer or a metal-based perovskite layer.

10. The hydrocarbon pyrolysis system as recited in any one of above claims, wherein the catalytic layer comprises at least one of: Nickel, Iron, Copper and Zinc, Cobalt, CeO_2 and La_2O_3 .

11. The hydrocarbon pyrolysis system as recited in any one of above claims, wherein the hydrogen purifying layer is a Pd layer, a Pd-alloy layer, a perovskite-based layer, a Ni Layer, a Ni-alloy layer, or a Pd-Ni-alloy layer.

12. The hydrocarbon pyrolysis system as recited in any one of above claims, wherein the support layer is an Al_2O_3 layer, a stainless steel layer, a MgO layer or a SiO_2 layer.

13. The hydrocarbon pyrolysis system as recited in any one of above claims, wherein each of the at least one catalytic membrane comprises at least one of: a disc structure and a tubular structure.

14. A hydrocarbon pyrolysis method, comprising:

maintaining a hydrocarbon in an interior chamber at an operating temperature to form hydrogen and carbon nanotubes simultaneously;

depositing the carbon nanotubes on a catalytic layer of at least one catalytic membrane, wherein each of the at least one catalytic membrane comprises a support layer disposed between the catalytic layer and a hydrogen purifying layer; and

concurrent to depositing the carbon nanotubes, selectively removing the hydrogen from the interior chamber with the at least one catalytic membrane, wherein the at least one catalytic membrane is carbon nanotube impermeable.

15. The hydrocarbon pyrolysis method as recited in claim 14, further comprising: recovering the carbon nanotubes using at least one of: a solvent-assisted method and a gas-phase fluidization method.

16. The hydrocarbon pyrolysis method as recited in any one of claims 14 and 15, further comprising: regenerating the catalytic layer by oxidizing carbon nanotubes on the catalytic layer with a mild oxidant at the operating temperature.

17. The hydrocarbon pyrolysis method as recited in claim 16, wherein the mild oxidant comprises at least one of: CO₂, air, and NO_x.

18. The hydrocarbon pyrolysis method as recited in any one of claims 14 to 17, further comprising: maintaining the operating temperature at a temperature range of between 400°C to 800°C.

19. The hydrocarbon pyrolysis method as recited in claim 18, wherein the temperature range is between 500°C to 650°C.

20. The hydrocarbon pyrolysis method as recited in any one of claims 14 to 19, wherein the hydrocarbon comprises at least one of: methane, ethane, propane and waste-derived tars.