(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 December 2009 (03.12.2009)

PCT

(10) International Publication Number
WO 2009/145936 A2

(51) International Patent Classification:
C09K 3/00 (2006.01)

(21) International Application Number:
PCT/US2009/034202

(22) International Filing Date:
16 February 2009 (16.02.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
12/040,883 1 March 2008 (01.03.2008) US

(71) Applicants *(for all designated States except US)*: **HYTHANE COMPANY LLC** [US/US]; 12420 N. Dumont Way, Littleton, CO 80125 (US). **UNIVERSITY OF QUEENSLAND** [AU/AU]; Brisbane, 4072 QLD (AU). **EDEN ENERGY LTD.** [AU/AU]; Level 40, Exchange Plaza, 2 The Esplande, Perth, W.A. 6000 (AU).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **ZHU, Zhonghua, John** [AU/AU]; 8 Serle St. Middle Park, Brisbane, QLD 4072 (AU). **CHEN, Jiuling** [CH/CH]; 1/39 Grosvenor Road, Indooroopilly, Brisbane, QLD 4078 (AU). **LU, Gaoqing, Max** [AU/AU]; 38 Debussy Place, Mt Ommaney, Brisbane, QLD 4072 (AU). **SOLOMON, Gregory** [AU/AU]; 7 Torrens Street, Cottesloe, Western Australia 6011 (AU).

(74) Agent: **GRATTON, Stephen, A.**; 2764 South Braun Way, Lakewood, CO 80228 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

(54) **Title**: METHOD FOR PRODUCING A HYDROGEN ENRICHED FUEL AND CARBON NANOTUBES USING MICROWAVE ASSISTED METHANE DECOMPOSITION ON CATALYST

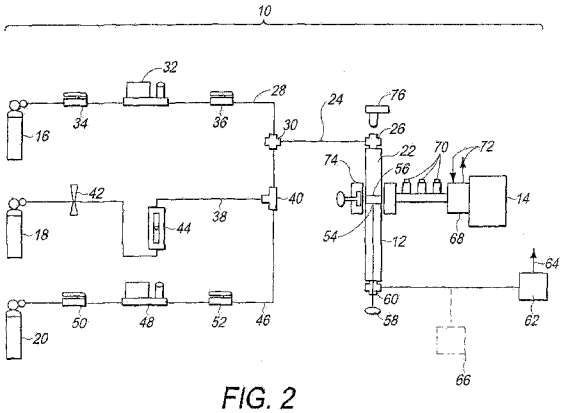


FIG. 2

(57) **Abstract**: A method for producing a hydrogen enriched fuel and carbon nanotubes includes the steps of providing a flow of methane gas (16), and providing a catalyst mixture (56) comprising a Fe based catalyst and carbon. The method also includes the steps of pretreating the catalyst mixture (56) using microwave irradiation and exposure to CH_4, heating the catalyst mixture (56) and the methane gas (16) using microwave irradiation at a selected microwave power, directing the flow of methane gas (16) over the catalyst mixture (56), and controlling the microwave power to produce a product gas having a selected composition and the carbon nanotubes. For producing multi walled carbon nanotubes (MWNTs) only a flow of methane gas (16) into the reactor (12) is required. For producing single walled carbon nanotubes (SWNTs), a combination of hydrogen gas (18) and methane gas into the reactor (12) is required.

WO 2009/145936 A2

METHOD FOR PRODUCING A HYDROGEN ENRICHED FUEL AND CARBON NANOTUBES USING MICROWAVE ASSISTED METHANE DECOMPOSITION ON CATALYST

Cross Reference To Related Applications

[0001] This application is a continuation in part of serial no. 11/657,212 filed on 01/24/2007.

Field of the Invention

[0002] This invention relates generally to the production of hydrogen fuels, and particularly to a method for producing a hydrogen enriched fuel suitable for use as an alternative fuel along with carbon nanotubes.

Background of the Invention

[0003] Gaseous alternative fuels, such as hydrogen and natural gas, are valued for their clean burning characteristics in motor vehicle engines. Various processes have been developed for producing hydrogen. These processes include electrolysis, exotic water splitting, and separation from industrial waste streams.

[0004] Hydrogen can also be produced by reforming natural gas. Typically, a multi-step process is used to convert a hydrocarbon fuel, such as methane, propane or natural gas, into a high purity hydrogen gas stream. The steps of the process typically include (1) synthesis gas generation, (2) water-gas shift reaction, and (3) gas purification (e.g., CO and CO_2 removal). The hydrogen gas stream can then be used for a variety of purposes including mixture with other gases to produce an alternative fuel.

[0005] For example, a particularly clean burning gaseous alternative fuel known as HYTHANE comprises a mixture of hydrogen and natural gas. The prefix "Hy" in HYTHANE is taken from hydrogen. The suffix "thane" in HYTHANE is taken from methane, which is the primary constituent of natural gas. HYTHANE is a registered trademark of Eden Innovations LLC. HYTHANE typically contains about 5% to 7% hydrogen by energy, which corresponds to 15% to 20% hydrogen by volume.

[0006] For producing hydrogen, one type of reformer called a "steam reformer" uses a hydrocarbon fuel and steam (H_2O). In the steam reformer, the hydrocarbon fuel is reacted in a heated reaction tube containing steam (H_2O) and one or more catalysts. In general, the production of a high purity hydrogen gas by reforming requires high temperatures (800-900 °C). Steam reforming also produces impurities, particularly CO and CO_2, which if not removed, are ultimately released to the atmosphere.

[0007] The production of a high purity hydrogen gas by reforming also requires large capital costs for the equipment, and large operating costs, particularly for power. In addition to these shortcomings, it is difficult to manufacture a compact embodiment of a steam reformer. It would be advantageous for a hydrogen production system to have a relatively compact size, such that alternative fuels could be produced at a facility the size of a gas station, rather than at a facility the size of a refinery.

[0008] Another process for producing hydrogen from natural gas involves the thermal decomposition of methane. For example, methane decomposes into hydrogen by the reaction:

$CH_4 = C + 2H_2$

For example, the thermal decomposition of natural gas has been used in the "Thermal Black Process" for producing carbon black and hydrogen. Using thermal decomposition, the energy requirements per mole of hydrogen produced (37.8 kJ/mol H_2) is considerably less than the energy requirements of the steam reforming process (63.3 kJ/mol H_2). However, the process still requires high temperatures (e.g., 1400 °C), high equipment costs, and high energy expenditures.

[0009] Recently, thermal decomposition of natural gas has been investigated in combination with various catalysts, which allow the reaction to proceed at lower temperatures. For example, US Patent No. 7,001,586 B2, to Wang et al. discloses a thermal decomposition process in which two catalysts having the formula Ni_xMg_yO and $Ni_xMg_yCu_zO$, respectively, are used to decompose methane to carbon and hydrogen. The former needs a lower temperature from about 425°C to 625°C, but the lifetime is shorter and the activity is lower. The latter's lifetime is longer and the activity is higher. However, because the energy for the reaction was provided by conventional heating, these processes require high energy expenditures to heat the wall of the reactor, the gas and the catalysts.

[0010] It would be advantageous for a hydrogen production system to be capable of performance at lower energy expenditures, with a variety of catalysts active for long periods, and with minimal carbon emissions (e.g., CO, CO_2). In addition, it would be advantageous for a hydrogen production system to have a size and configuration adaptable to the production of alternative fuels containing hydrogen. The present disclosure is directed to a method and a system for producing a hydrogen enriched fuel that overcomes many of the shortcomings of prior art hydrogen production systems.

[0011] The foregoing examples of the related art and limitations related therewith are intended to be illustrative and not exclusive. Other limitations of the related art will become apparent to those of skill in the art upon a reading of the specification and a study of the drawings. Similarly, the following embodiments and aspects thereof are described and illustrated in conjunction with a system and method, which are meant to be exemplary and illustrative, not limiting in scope.

Summary of the Invention

[0012] A method for producing a hydrogen enriched fuel includes the steps of providing a flow of methane gas, providing a catalyst, selectively heating the catalyst instead of the reactor walls and the methane gas using microwave irradiation at a selected microwave power, directing the flow of methane gas over the catalyst, and controlling the microwave power to produce a product gas having a selected composition.

[0013] The method can be performed in a reactor having a reaction chamber with microwave transparent walls. In addition, the catalyst can comprise a metal, such as a Ni-based compound prepared by coprecipitation. On the surface of the catalyst reactions occur in which methane (CH_4) dissociates into hydrogen (H_2) and solid carbon (C) in the form of fibrous carbon. In addition, some of the methane gas fails to react (methane slip) such that the product gas comprises methane and hydrogen. The catalyst is selected and formulated to remain stable under operating conditions (e.g., gas flow rate, microwave power, catalyst amount), such that costs are minimized. In addition, the catalyst maintains active characteristics through many hours of reactions.

[0014] The flow of methane gas and the microwave power can be controlled such that the composition of the product gas approximates the chemical composition

of HYTHANE. For example, the product gas can comprise from about 20% to 30% hydrogen by volume, and from about 70% to 80% methane by volume. Advantageously, the product gas contains almost no carbon impurities (e.g., CO, CO_2), as carbon is converted to solid fibrous carbon which drops out of the product gas as a useful by-product. In addition, the product gas contains only negligible amounts of higher order hydrocarbons (e.g., C_2H_4, C_2H_2, C_3H_6, C_3H_8, C_3H_4).

[0015] A system for producing a hydrogen enriched fuel includes a methane gas source configured to provide a methane gas flow. The system also includes a reactor having a reaction chamber in flow communication with the methane gas source configured to contain a catalyst, and to circulate the methane gas in contact with the catalyst. The system also includes a microwave power source configured to heat the catalyst in the reaction chamber to form a product gas having a selected volumetric percentage of hydrogen and methane.

[0016] In an alternate embodiment of the method, the product gas is further processed to recover hydrogen in substantially pure form. To recover substantially pure hydrogen, the product gas can be flowed under a vacuum through a Pd/Ag membrane coated on a porous metal or ceramic plate.

[0017] In another alternate embodiment of the method, both a hydrogen enriched fuel and carbon nanotubes (CNTs) are produced. For producing both a hydrogen enriched fuel and carbon nanotubes (CNTs), the catalyst comprises a mixture of an Fe-based compound and carbon, which is pretreated in the reactor by microwave irradiation in the presence of CH_4 or H_2 for one to several minutes. For producing multi walled carbon nanotubes (MWCNs) only a flow of methane gas into the reactor is required. For producing single walled carbon nanotubes (SWCNs), a combination of hydrogen gas and methane gas into the reactor are required.

Brief Description of the Drawings

[0018] Exemplary embodiments are illustrated in the referenced figures of the drawings. It is intended that the embodiments and the figures disclosed herein are to be considered illustrative rather than limiting.

[0019] Figure 1 is a flow diagram illustrating steps in a method for producing a hydrogen enriched fuel;

[0020] Figure 2 is a schematic drawing of a system for producing a hydrogen enriched fuel;

[0021] Figure 3 is an overlaid graph illustrating CH_4 conversion, H_2 content, and carbon formation versus reaction time for Example 1 using a Ni54Cu27Al catalyst;

[0022] Figure 4 is an overlaid graph illustrating CH_4 conversion, H_2 content, and carbon formation versus reaction time for Example 2 using a Ni81Al catalyst;

[0023] Figure 5 is an overlaid graph illustrating carbon formation, H_2 content and CH_4 conversion for an alternate embodiment method of Example 3 in which both a hydrogen enriched fuel and carbon nanotubes are produced;

[0024] Figure 6 is a transmission electron microscopic image illustrating carbon nanotubes produced by the method of Example 3;

[0025] Figure 7 is an overlaid graph illustrating carbon formation, H_2 content and CH_4 conversion for an alternate embodiment method of Example 4 in which both a hydrogen enriched fuel and carbon nanotubes are produced;

[0026] Figure 8A is a transmission electron microscopic image illustrating carbon nanotubes produced by the method of Example 4;

[0027] Figure 8B is a transmission electron microscopic image illustrating a carbon nanotube produced by the method of Example 4;

[0028] Figure 9 is an overlaid graph illustrating carbon formation, H_2 content and CH_4 conversion for an alternate embodiment method of Example 5 in which both a hydrogen enriched fuel and carbon nanotubes are produced;

[0029] Figure 10A is a transmission electron microscopic image illustrating carbon nanotubes produced by the method of Example 5; and

[0030] Figure 10B is a transmission electron microscopic image illustrating carbon nanotubes produced by the method of Example 5.

Detailed Description of the Preferred Embodiments

[0031] The following definitions are used in the present disclosure. HYTHANE means a hydrogen enriched alternative fuel comprised of hydrogen and methane and impurities included in hydrogen and natural gas.

[0032] Methane slip means unreacted methane which passes through a system without reacting.

[0033] Microwave irradiation means electromagnetic irradiation in the range of 0.3 to 300 GHz.

[0034] Carbon nanotubes (CNTs) are allotropes of carbon having a nanostructure where the length to diameter ratio exceeds 1,000,000. The diameter of a carbon nanotube (CNT) is on the order of a few nanometers, while the length is on the order of millimeters. Carbon nanotubes (CNTs) are generally cylindrical in shape and have a fullerene cap. Carbon nanotubes (CNTs) can have a single wall or multiple walls. A single walled nanotube (SWNT) can have a diameter of close to 1 nanometer. A multi walled nanotube (MWNT) includes multiple layers of graphite rolled in on themselves to form a tube shape. Single walled nanotubes (SWNTs) are generally preferred for most applications because they have fewer defects and are stronger and more conductive than multi walled nanotubes (MWNTs). Carbon nanotubes (CNTs) can be used for a variety of applications including nanoscale electronic devices, high strength materials, field emission devices, and gas storage.

Method

[0035] Referring to Figure 1, steps in a method for producing a hydrogen enriched fuel are illustrated. The first step comprises "providing a flow of methane gas at a selected flow rate". By way of example, the methane gas can be in the form of pure methane gas. Alternately, the methane gas can be in the form of natural gas obtained from a "fossil fuel" deposit. Natural gas is typically about 90+% methane, along with small amounts of ethane, propane, higher hydrocarbons, and "inerts" like carbon dioxide or nitrogen. In addition, the methane gas can be supplied from a tank (or a pipeline) at a selected temperature and pressure. Preferably, the methane gas is provided at about room temperature (20 to 25 °C), and at about atmospheric pressure (1 atmosphere). Further, the methane gas can be provided at the selected flow rate. In the examples to follow, the selected flow rate of the methane gas is about 120 ml/minute (STP).

[0036] As also shown in Figure 1, the method includes the step of "providing a catalyst". Preferably, the catalyst is provided in the form of particles having a diameter of from 74 μm to 140 μm. In addition, the catalyst is preferably contained on a holder, which allows the methane gas to flow freely along the surfaces of the catalyst particles. In addition, catalysts in the form of metal oxides can be pre-treated using H_2 to reduce the metal oxide to a metal.

[0037] A preferred metal for the catalyst comprises Ni, or an alloy containing Ni. For example, the metal can comprise NiAl, or Ni doped with Cu, Pd, Fe, Co, or an oxide such as MgO, ZnO, Mo_2O_3 or SiO_2. Specific catalysts include Ni81Al, Ni93Al, Ni77Cu16Al, Ni54Cu27Al and Ni83Mg6Al. In addition, nickel based catalyst precursors can be prepared by coprecipitation from a mixed aqueous solution of nitrates with sodium carbonate.

[0038] The following Table I provides information on catalyst preparation of nickel-based precursors for the above catalysts. These catalysts were prepared by coprecipitation from a mixed aqueous solution of nitrates with sodium carbonate.

Table 1-Catalyst Preparation

Catalyst Composition

1	Ni81Al	81 wt.%NiO-19 wt.%Al_2O_3
2	Ni93Al	93 wt. %NiO-7 wt.%Al_2O_3
3	Ni77Cu16Al	77 wt.%NiO-16wt.%CuO-7 wt.%Al_2O_3
4	Ni54Cu27Al	54 wt.%NiO-27 wt.%CuO-9 wt.%Al_2O_3
5	Ni83Mg6Al	83 wt.%NiO-6 Wt.%MgO-11 wt.%Al_2O_3

[0039] However, rather than Ni or an alloy thereof, the catalyst can comprise another metal, such as a metal selected from group VIII of the periodic table including Fe, Co, Ru, Pd and Pt. In any case the catalyst is selected and formulated to remain stable under reaction conditions for long periods of time. In the examples to follow there was no indication that the catalyst was going to be deactivated, even after over 16 hours of reaction time.

[0040] As also shown in Figure 1, the method includes the step of "heating the catalyst using microwave irradiation at a selected microwave power". This step can be performed using a conventional microwave generator and microwave circulator configured to irradiate the catalyst with microwave irradiation. In general, microwave energy selectively heats the metal catalyst instead of the reactor wall and the methane gas, thus significantly saving the energy consumption of the catalyst/microwave heating process.

[0041] Heating the catalyst by microwave irradiation provides the following advantages:

a.) volumetric heating, fast,

b.) selectively heating the catalyst instead of the reactor wall and the methane gas, high efficiency,

c.) low temperature gradient,

d.) hot spot to prevent serial reaction of product,

e.) may also influence catalytic reaction by changing the electronic properties of the catalyst in the microwave electromagnetic field.

[0042] In the examples to follow, the microwave generator was operated at a power of about 250 watts, and the catalyst was heated to a temperature of from about 600 to 700 °C. However, it is to be understood that the method can be practiced at a microwave power that is selected to achieve a desired product gas composition. For example, a representative range for the microwave power can be from 150 watts to 300 watts. Also in the examples to follow, the microwave generator was operated at a frequency of 2.45 GHz. For performing microwave irradiation, the reactor and the holder for the catalyst must be made of a microwave transparent material able to withstand high temperatures. One suitable material for the reactor and the holder comprises quartz.

[0043] As also shown in Figure 1, the method includes the step of "directing the flow of methane gas over the catalyst". This step can be performed by placing the catalyst in a microwave transparent reactor having a reaction chamber configured to contain the catalyst, and to direct the flow of methane gas over the catalyst.

[0044] As also shown in Figure 1, the method includes the step of "controlling the microwave power at the selected flow rate to produce a product gas having a selected composition". This step can be performed using a microwave generator having variable power controls.

System

[0045] Referring to Figure 2, a system 10 for producing a hydrogen enriched fuel, in accordance with the previously described method, is illustrated. The system 10 includes a reactor 12, and a microwave generator 14. The system also includes a methane supply 16, a hydrogen supply 18, and an inert gas supply 20 in flow communication with the reactor 12.

[0046] The reactor 12 (Figure 2) can comprise a conventional tube reactor made of a microwave transparent material, such as quartz. In addition, the reactor 12 includes a sealed process chamber 22 having an inlet 26 in flow communication with a supply conduit 24.

[0047] The supply conduit 24 (Figure 2) is in flow communication with a methane conduit 28 via a union 30, which is in flow communication with the methane supply 16. In addition, the methane conduit 28 includes a methane mass flow controller 32 configured to remotely control the flow of methane gas into the reaction chamber 22, and shut off valves 34, 36 on either side of the methane mass flow controller 32. In the illustrative embodiment, the methane supply 16 is configured to provide pure methane. However, it is to be understood that the system 10 can include, and the method can be practiced, using another methane source, such as natural gas.

[0048] The supply conduit 24 (Figure 2) is also in flow communication with a hydrogen conduit 38 via a union 40, which is in flow communication with the hydrogen gas supply 18. The hydrogen conduit 38 includes a needle valve 42 configured to manually regulate the flow of hydrogen gas into the reaction chamber 22, and a rotameter 44 configured to measure the hydrogen flow.

[0049] The supply conduit 24 (Figure 2) is also in flow communication with an inert gas conduit 46, which is in flow communication with the inert gas supply 20. The inert gas can comprise Ar or another inert gas, such as He or Ne. The inert gas conduit 46 also includes an inert gas mass flow controller 48 configured to remotely control the flow of inert gas into the reaction chamber 22, and shut off valves 50, 52 on either side of the inert gas mass flow controller 48. The inert gas conduit 46 can be used to purge the reaction chamber 22.

[0050] In addition to the reaction chamber 22 (Figure 2), the reactor 12 includes a holder 54 configured to hold a catalyst 56 in the reaction chamber 22. As with the reactor 12 and the walls of the reaction chamber 22, the holder 54 is made of a microwave transparent material. In addition, the holder 54 has a cup like configuration with openings that permit gas flow through the holder 54 and around the catalyst 56. The holder 54 also includes a handle 58 configured to permit removal of the holder 54 and the catalyst 56 from the reaction chamber 22.

[0051] The reactor 12 (Figure 2) also includes an outlet 60 in flow communication with the reaction chamber 22. The outlet 60 of the reactor 12 is

configured to exhaust the product gas formed in the reaction chamber 22. The outlet 60 is in flow communication with a gas chromatograph 62 configured to analyze the chemical composition of the product gas exiting the reaction chamber 22. In addition, the gas chromatograph 62 is in flow communication with a vent 64 configured to vent product gases, which have been analyzed to the atmosphere. The outlet 60 of the reactor 12 can also be in flow communication with a product gas storage vessel 66 configured to store the product gas for future use.

[0052] The microwave generator 14 (Figure 2) of the system 10 is configured to direct microwave radiation through a microwave circulator 68, and through a three stub tuner 70, to the catalyst 56 held on the holder 54 in the reaction chamber 22. The microwave circulator 68 also includes a cooling system 72. In addition, a microwave adjust plug 74 is configured to remotely adjust the reflected power of the microwave generator 14.

[0053] The system 10 (Figure 2) also includes an infrared temperature sensor 76 configured to measure the temperature of the catalyst 56.

Example 1

[0054] Using the previously described method (Figure 1), and the previously described system 10 (Figure 2), a hydrogen enriched fuel comprising CH_4 and H_2 was produced under the following conditions.

A. Pure methane gas (99.7% purity) was supplied through the methane supply conduit 28 to the reactor 12 (Figure 2).

B. Methane flow rate (i.e., selected flow rate in Figure 1): 120 ml/minute.

C. Catalyst 56 (Figure 2): Ni54Cu27Al.

D. The catalyst 56 (Figure 2) was initially reduced for a period of several minutes in H_2 plasma at a microwave power of 160 W. For reducing the catalyst 56 (Figure 2), a flow of H_2 gas was supplied through the hydrogen supply conduit 38 (Figure 2) to the reaction chamber 22 (Figure 2), and irradiated with microwave energy from the microwave generator 14 (Figure 2) to form a plasma.

E. Reaction pressure: atmospheric pressure (1 atm).

F. Products (hydrogen enriched fuel): H_2, solid carbon C and unreacted CH_4, by the reaction $CH_4 = C + 2H_2$. SEM (scanning electron microscopy) pictures of the solid carbon demonstrate that the carbon is in the form of fibrous carbon rather than

carbon black. In addition, the fibrous carbon is a useful by-product that can be used for other applications.

G. Microwave power applied to the catalyst: 250W.

H. Methane conversion: approximately 20%.

I: Unreacted methane: approximately 80%.

J. Production rate: about 48 ml/minute of H_2 at stable conditions.

K. In Example 1 the only energy consumed was in heating the catalyst. Accordingly the process is energy efficient.

[0055] Figure 3 illustrates the results of CH_4 conversion assisted by microwave heating using Ni54Cu27Al as the catalyst 56 (Figure 2). Example 1 was a continuous process. In Figure 3, the reaction time in hours (h) denotes the length of time that the process was performed.

[0056] In Figure 3 there are three separate graphs. The lower graph plots the conversion rate "X %" of the CH_4 on the y-axis (expressed as a volume percentage) versus the reaction time in hours on the x-axis. The middle graph plots the content "C %" of H_2 on the y-axis (expressed as a volume percentage) versus the reaction time in hours on the x-axis. The upper graph plots the amount of solid carbon (Solid C (g)) on the y-axis (expressed in grams) versus the reaction time in hours on the x-axis.

Example 2

[0057] Example 2 was performed using the same conditions as outlined above for Example 1 but with the catalyst comprising Ni81Al rather than Ni54Cu27Al.

[0058] Figure 4 illustrates the results of CH_4 conversion assisted by microwave heating using Ni81Al as the catalyst 56 (Figure 2). Example 2 was a continuous process. In Figure 4, the reaction time in hours (h) denotes the length of time that the process was performed.

[0059] In Figure 4 there are three separate graphs. The lower graph plots the conversion rate "X %" of the CH_4 on the y-axis (expressed as a volume percentage) versus the reaction time in hours on the x-axis. The middle graph plots the content "C %" of H_2 on the y-axis (expressed as a volume percentage) versus the reaction time in hours on the x-axis. The upper graph plots the amount of solid carbon (Solid C (g))on the y-axis (expressed in grams) versus the reaction time in hours on the x-axis.

[0060] From these two examples it was determined that a product gas containing 30% by volume of H_2 can be produced continuously and stably by microwave heating a Ni54Cu27Al catalyst. A product gas containing 20% by volume of H_2 can be produced continuously and stably by microwave heating a Ni81Al catalyst.

Alternate Embodiment Method For Producing Pure Hydrogen

[0061] An alternate embodiment of the method includes the additional step of further processing the product gas to recover hydrogen in substantially pure form. One method for recovering pure hydrogen is to flow the product gas under a vacuum through a Pd/Ag membrane coated on a porous metal or ceramic substrate. US Patent No. 6,165,438, to Willms et al., which is incorporated herein by reference, discloses an apparatus and method for the recovery of hydrogen from a gas containing hydrocarbons.

Alternate Embodiment Method For Producing Both A Hydrogen Enriched Fuel and Carbon Nanotubes (CNTs)

[0062] Another alternate embodiment of the method produces both a hydrogen enriched fuel and carbon nanotubes (CNTs). This method requires the use of a catalyst mixture which includes an Fe based catalyst mixed with carbon. In addition, this method requires that the catalyst be pretreated in the reaction chamber 12 (Figure 2) using microwave irradiation and exposure to CH_4 or H_2. Examples 3-5 to follow employ this method. Examples 3 and 4 produce multi walled carbon nanotubes (MWNTs). Example 5 produces single walled carbon nanotubes (SWNTs). For producing single walled carbon nanotubes (SWNTs), the method also requires that the feed gas into the reactor 12 (Figure 2) includes both a methane gas and a pure hydrogen gas.

[0063] Catalyst samples for Examples 3-5 were prepared by the coprecipitation method. Catalyst samples employed and their composition are shown in Table 2.

Table 2, Catalyst samples and their composition

Catalyst samples	Composition

FeAl	61 wt.%Fe_2O_3-39 wt.%Al_2O_3
Fe3Al	82 wt.%Fe_2O_3-18 wt.%Al_2O_3
Fe2CuAl	56 wt.%Fe_2O_3-26 wt.%CuO-18 wt.% Al_2O_3
Fe2NiAl	55 wt.%Fe_2O_3-27 wt.%CuO-18 wt.% Al_2O_3
1.2wt%Fe_2O_3/MgO	1.2 wt.% Fe_2O_3-98.8 wt.% MgO

[0064] Feed gases.

a. In Examples 3 and 4 for producing multi walled carbon nanotubes (MWNTs), a feed gas in the form of CH_4 at a flow rate of 120ml/min was used.

b. In Example 5 for producing single walled carbon nanotubes (SWNTs), a feed gas included a mixture of CH_4 at a flow rate of 60 ml/min combined with H_2 at a flow rate of 60 ml/min.

[0065] The catalysts in Examples 3-5 were subjected to a pretreatment step performed in the reactor 12 (Figure 2). Catalyst samples were in an oxide state, and during pretreatment, were mixed with carbon and reduced with CH_4 or H_2. The catalyst mixture was induced at a higher microwave forward power (300-1000 W), followed by reduction at a lower power (200 to 450 W) in the presence of CH_4 or H_2. Vacuum is not needed for the pre-treatment, as atmosphere pressure can be employed.

[0066] The following operating conditions were employed in Examples 3-5.

Reaction pressure: atmosphere pressure.

Forward power for reaction: 220-650 W.

Sample amount: mixture of 600 mg catalyst and 400 mg solid carbon.

System 10 (Figure 2) is configured as previously described.

Example 3 For Producing A Hydrogen Enriched Fuel and Multi Walled Carbon Nanotubes (MWNTs)

[0067] Steps:

(1) 600 mg of Fe3Al catalyst was mixed with 400 mg of solid carbon, then the mixture was moved to the catalyst quartz holder.

(2) Pretreatment: the catalyst mixture (catalyst and carbon) was firstly induced at 500 W forward power for a couple of minutes, followed by reduction at 325 W in the presence of CH_4.

(3) Reaction: the power was controlled in the range of 325-365 W for the reaction and the temperature was kept around 850-900 ^{O}C. The feed gas was pure CH_4. The flow rate was 120 ml/min.

[0068] Figure 5 illustrates the results of the method of Example 3 for producing a hydrogen enriched fuel and multi walled carbon nanotubes (MWNTs) from methane decomposition using microwave heating and an Fe_3Al catalyst. In Example 3, the weight of the catalyst was 600 mg; the weight of the catalyst mixture was 1000 mg; the flow rate of pure CH_4 was 120 ml/minute; the microwave power output was 325-365 W. In Figure 5, X_{CH4} represents the CH_4 conversion, C_{H2} represents the H_2 volume percentage in the outlet gas, and Solid C represents carbon formation in grams. Figure 6 illustrates the multi walled carbon nanotubes (MWNTs) produced by the method of Example 3.

[0069] At the beginning of Example 3, the conversion of CH_4 was about 35% and a product gas containing about 52% H_2 could be obtained, then after 2 hours, the conversion of CH_4 decreased to about 8% and the H_2 content of the corresponding product gas was about 15%. The conversion of CH_4 could be maintained at about 8% for about 2 hours and then decreased again. The solid carbon produced in these conditions included multi-walled carbon nanotubes (MWNT) having a diameter between about 10-40 nm.

Example 4 For Producing A Hydrogen Enriched Fuel and Multi Walled Carbon Nanotubes (MWNTs)

[0070] Steps:

(1) A catalyst mixture of 600 mg of Fe_2NiAl catalyst and 400 mg of solid carbon was placed into the catalyst quartz holder.

(2) Pretreatment: the catalyst mixture (catalyst with carbon) was firstly induced at 300 W forward power for a couple of minutes, followed by reduction at 220 W in the presence of CH_4.

(3) Reaction: the power was controlled in the range of 220-300 W for the reaction and the temperature was kept around 750-850 ^{O}C. The feed gas was pure CH_4. The flow rate was 120 ml/min.

[0071] Figure 7 illustrates the results of the method of Example 4 for producing a hydrogen enriched fuel and multi walled carbon nanotubes (MWNTs) from methane decomposition using microwave heating and an Fe2NiAl catalyst. In

Example 4, the weight of the catalyst was 600 mg; the weight of the catalyst mixture was 1000 mg; the flow rate of pure CH_4 was 120 ml/minute; the microwave power output was 220-300 W. In Figure 7, X_{CH4} represents the CH_4 conversion, C_{H2} represents the H_2 volume percentage in the outlet gas, and Solid C represents carbon formation in grams. Figures 8A and 8B illustrate the multi walled carbon nanotubes (MWNTs) produced by the method of Example 4.

[0072] At the beginning of Example 4, the conversion of CH_4 was about 33% and a product gas containing about 50% H_2 could be obtained, then after 5 hours, the conversion of CH_4 decreased to about 10% and the H_2 content of the corresponding product gas was about 18%. The conversion of CH_4 could be maintained at about 10% for about 15 hours and then decreased again. The solid carbon produced in these conditions included multi-walled carbon nanotubes (MWNT) having a diameter between about 10-40 nm.

Example 5 For Producing A Hydrogen Enriched Fuel and Single Walled Carbon Nanotubes (SWNTs)

[0073] Steps:

(1) A catalyst mixture of 600 mg of 1.2wt%Fe_2O3/MgO catalyst and 400 mg of solid carbon was placed into the catalyst quartz holder.

(2) Pretreatment: the catalyst mixture (catalyst with carbon) was firstly induced at 500 W forward power for a couple of minutes, followed by reduction at 430 W in the presence of CH_4/H_2 at a volumetric ratio of 1:1.

(3) Reaction: the power was controlled in the range of 430-650 W for the reaction and the temperature was kept around 900-1000 ^{O}C. The feed gas was a mixture of CH_4/H_2 at a volumetric ratio of 1:1. The total flow rate was 120 ml/min.

[0074] Figure 9 illustrates the results of the method of Example 5 for producing a hydrogen enriched fuel and single walled carbon nanotubes (SWNTs) from methane decomposition using microwave heating and a 1.2wt%Fe_2O_3/MgO catalyst. In Example 5, the weight of the catalyst was 600 mg; the weight of the catalyst mixture was 1000 mg; the flow rate of pure CH_4 was 60 ml/minute; the flow rate of pure H_2 was 60 ml/minute; the microwave power output was 430-650 W. In Figure 9, X_{CH4} represents the CH_4 conversion, C_{H2} represents the H_2 volume percentage formed from CH_4 decomposition in the outlet gas, and Solid C represents carbon formation in

grams. Figures 9A and 9B illustrate the single walled carbon nanotubes (SWNTs) produced by the method of Example 5.

[0075] At the beginning of Example 5, the conversion of CH_4 was about 2.5% and a product gas containing about 5% H_2 could be obtained, then after 0.5 hours, the conversion of CH_4 decreased to about 0.3% and the H_2 content of the corresponding product gas was about 0.005%. The solid carbon produced in these conditions included single walled carbon nanotubes (SWNTs) having a diameter between about 5-30 nm.

[0076] Thus the disclosure describes an improved method and system for producing a hydrogen enriched fuel. While the description has been with reference to certain preferred embodiments, as will be apparent to those skilled in the art, certain changes and modifications can be made without departing from the scope of the following claims.

WHAT IS CLAIMED IS:

1. A method for producing a hydrogen enriched fuel and carbon nanotubes comprising:

providing a flow of methane gas;

providing a catalyst mixture comprising a Fe based catalyst and carbon;

pretreated the catalyst mixture using microwave irradiation and exposure to CH_4;

heating the catalyst mixture using microwave irradiation at a selected microwave power;

directing the flow of methane gas over the catalyst mixture; and

controlling the microwave power to produce a product gas having a selected composition and the carbon nanotubes.

2. The method of claim 1 wherein the carbon nanotubes comprise multi walled nanotubes (MWNTs).

3. The method of claim 1 further comprising providing a flow of a hydrogen gas in combination with the methane gas, and wherein the carbon nanotubes comprise single walled carbon nanotubes (SWNTs).

4. The method of claim 1 wherein the providing step provides the methane gas at about room temperature and at about 1 atmosphere.

5. The method of claim 1 wherein the catalyst comprises a compound selected from the group consisting of FeAl; Fe_3Al, Fe_2CuAL, Fe_2NiAl, and Fe_2O_3/MgO.

6. The method of claim 1 wherein the product gas comprises about 15% to 20% hydrogen by volume, and from about 80% to 85% methane by volume.

7. A method for producing a hydrogen enriched fuel and carbon nanotubes comprising:

providing a flow of methane gas and a flow of a hydrogen gas;

providing a catalyst mixture comprising a Fe based catalyst and carbon;

pretreated the catalyst mixture using microwave irradiation and exposure to CH_4;

heating the catalyst mixture using microwave irradiation at a selected microwave power;

directing the flow of methane gas and the flow of the methane gas over the catalyst mixture; and

controlling the microwave power to produce a product gas having a selected composition and single walled carbon nanotubes (SWNTs).

8. The method of claim 7 wherein the flow of methane gas and the flow of hydrogen gas are providing in a ratio of one to one.

9. The method of claim 7 wherein the catalyst comprises a compound selected from the group consisting of FeAl; Fe_3Al, Fe_2CuAL, Fe_2NiAl, and Fe_2O_3/MgO.

10. The method of claim 7 wherein the product gas comprises about 15% to 20% hydrogen by volume, and from about 80% to 85% methane by volume.

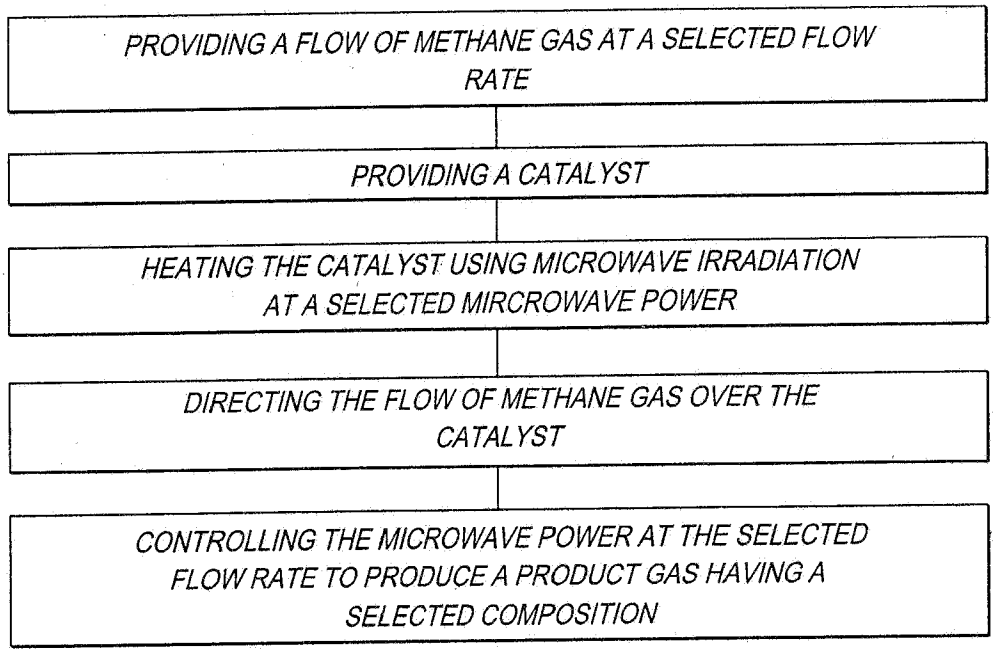

PROVIDING A FLOW OF METHANE GAS AT A SELECTED FLOW RATE
PROVIDING A CATALYST
HEATING THE CATALYST USING MICROWAVE IRRADIATION AT A SELECTED MIRCROWAVE POWER
DIRECTING THE FLOW OF METHANE GAS OVER THE CATALYST
CONTROLLING THE MICROWAVE POWER AT THE SELECTED FLOW RATE TO PRODUCE A PRODUCT GAS HAVING A SELECTED COMPOSITION

FIG. 1

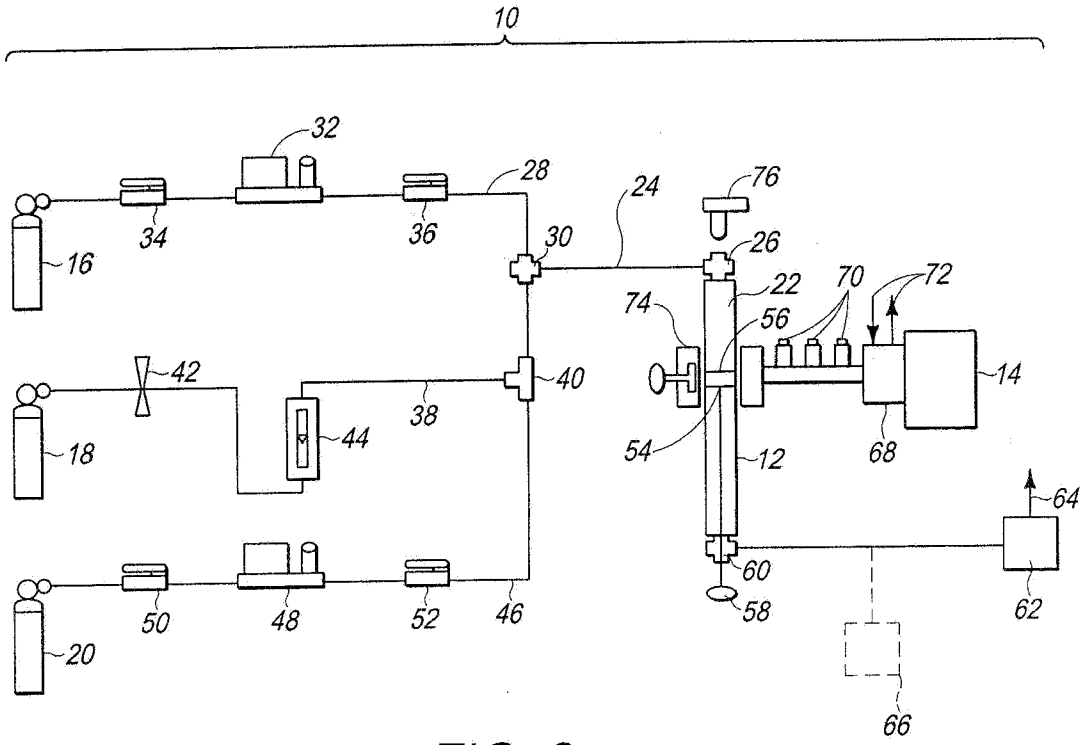

10
32
28
24
76
34
36
30
26
16
22
70
72
74
56
42
40
14
38
18
44
54
12
68
64
60
58
62
50
48
52
46
20
66

FIG. 2

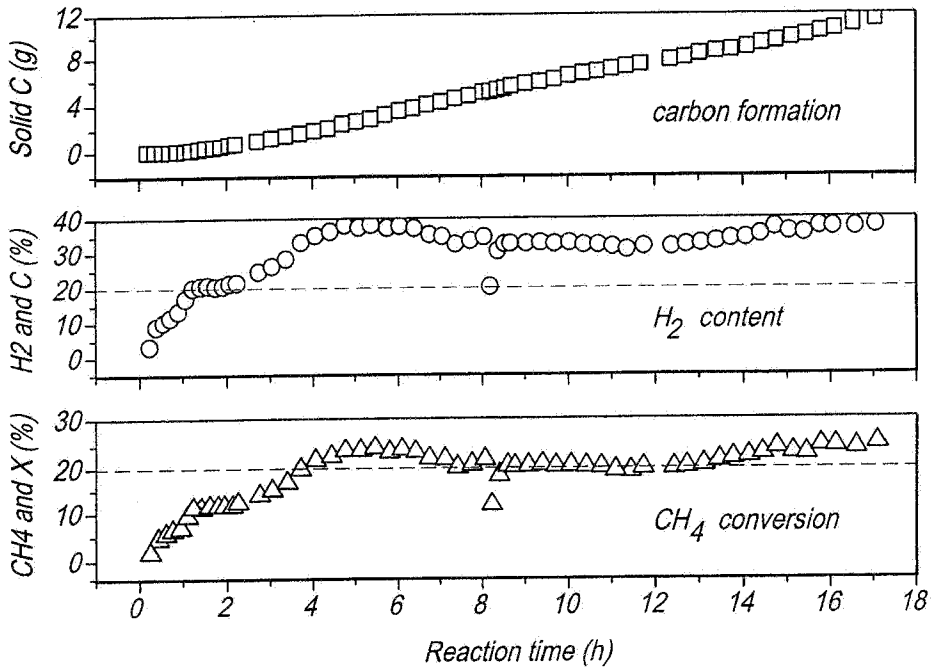

Solid C (g)
12
8
4
0
carbon formation
H2 and C (%)
40
30
20
10
0
H_2 content
CH4 and X (%)
30
20
10
0
CH_4 conversion
0
2
4
6
8
10
12
14
16
18
Reaction time (h)

FIG. 3

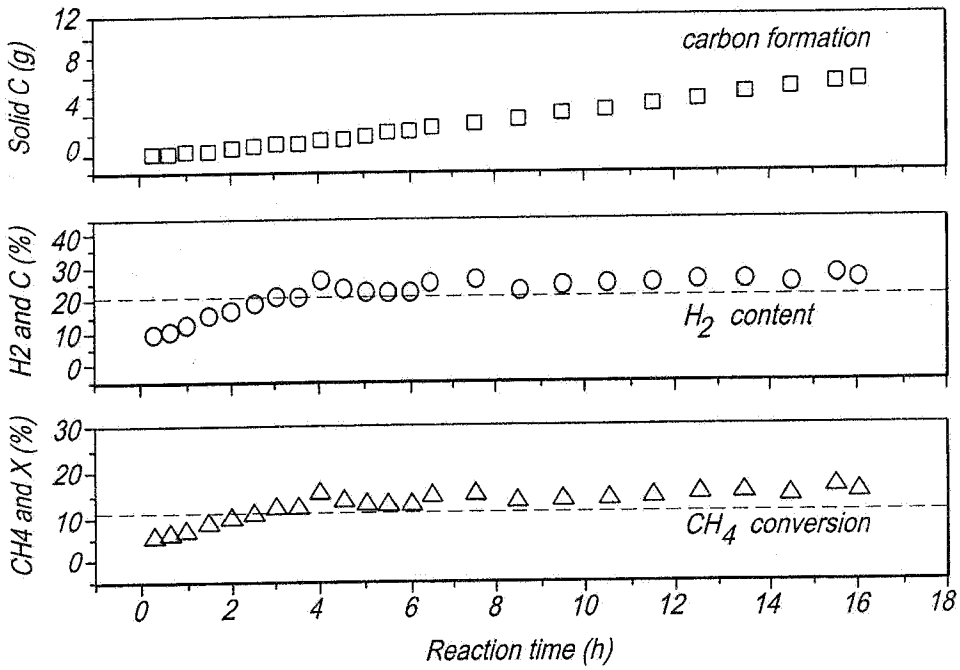

Solid C (g)
carbon formation
H2 and C (%)
H_2 content
CH4 and X (%)
CH_4 conversion
Reaction time (h)

FIG. 4

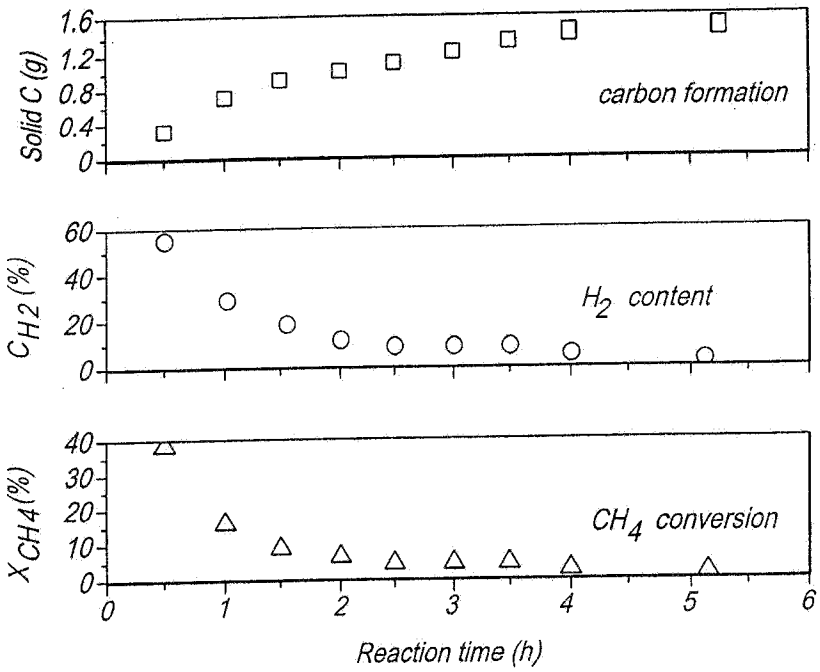

Solid C (g)
1.6
1.2
0.8
0.4
0
carbon formation
C_{H2} (%)
60
40
20
0
H_2 content
X_{CH4} (%)
40
30
20
10
0
CH_4 conversion
0
1
2
3
4
5
6
Reaction time (h)

FIG. 5

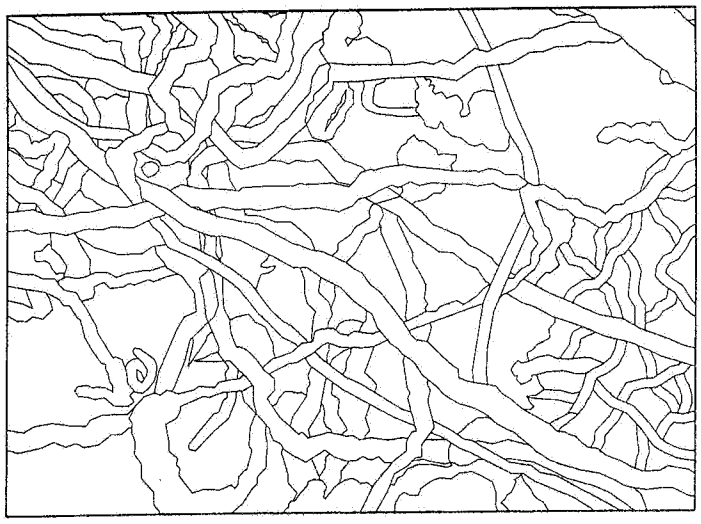


FIG. 6

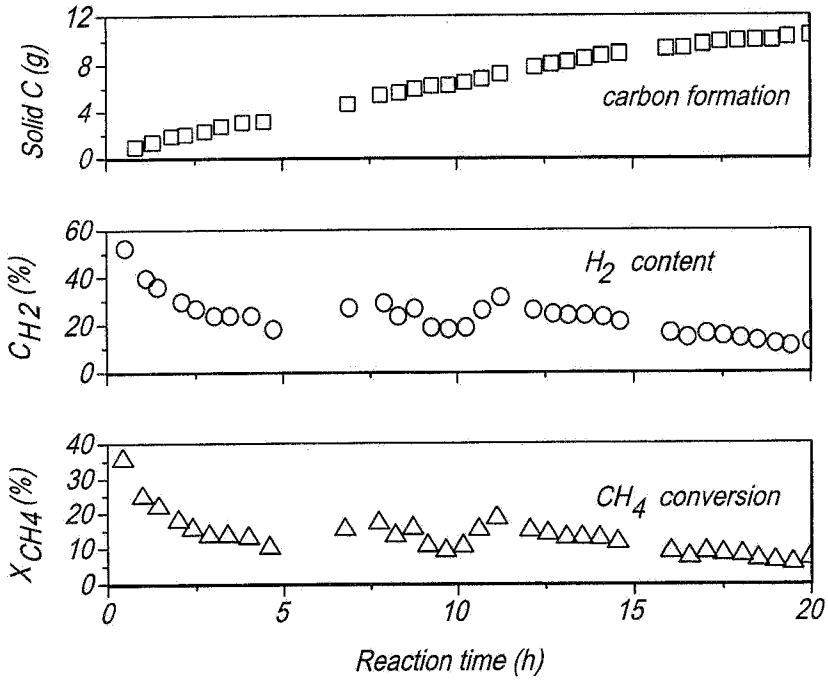


FIG. 7



FIG. 8A

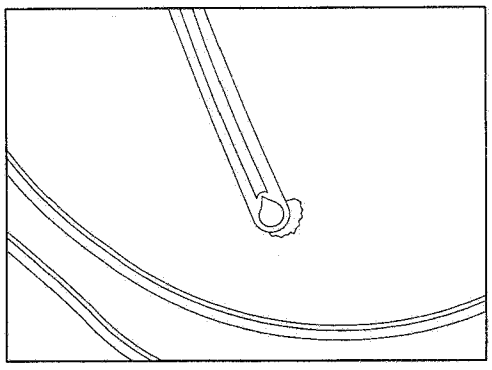


FIG. 8B

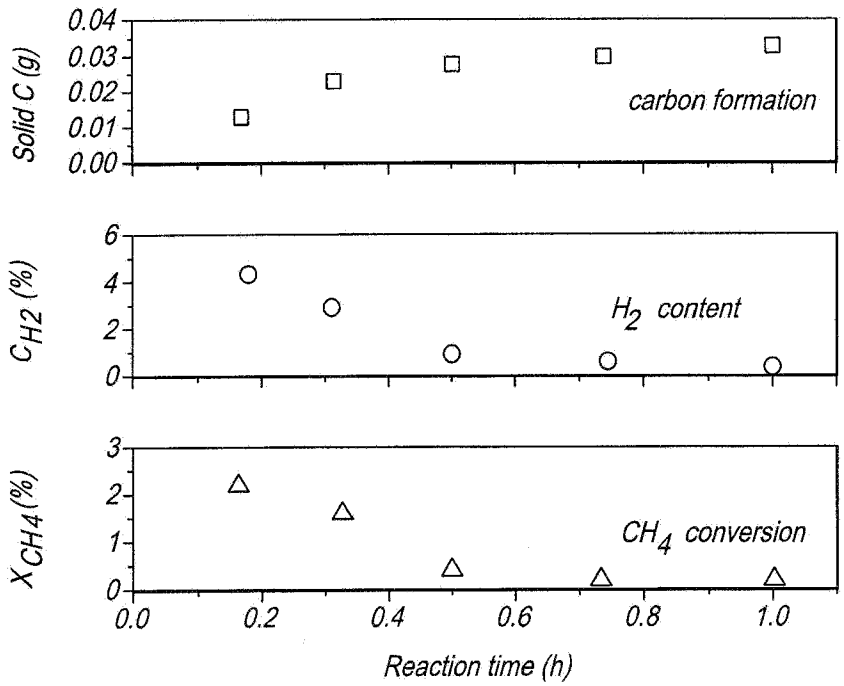


FIG. 9

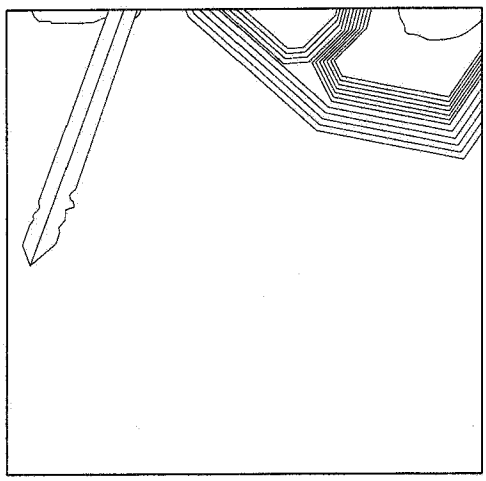


FIG. 10A

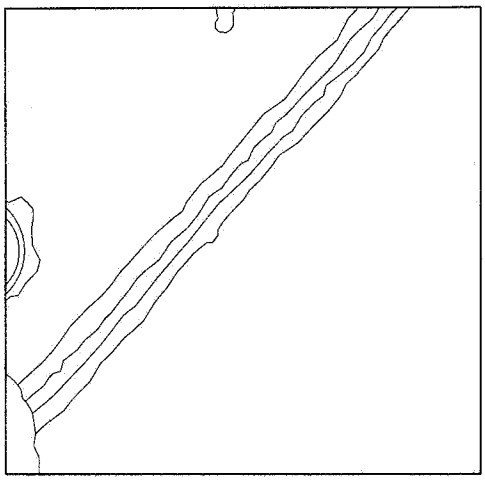


FIG. 10B