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Hydrogen Production via Methane Pyrolysis: An Overview of 'Turquoise' Hydrogen

November 1, 2023 | By Carl Fromm, Green Start BCS LLC

'Turquoise' hydrogen processes generate H_2 without releasing CO_2. Presented here are the opportunities and challenges for producing hydrogen by methane pyrolysis

Hydrogen-producing processes are classified using a color scheme according to their carbon footprint (Table 1; [1–3]). So-called "turquoise hydrogen" is produced by methane decomposition, which encompasses the following: thermal breakdown of molecular bonds (pyrolysis); non-thermal breakdown using non-thermal plasma (plasmalysis); radiation (photolysis); and chemical splitting (chemolysis) through halogenation or $NiCl_2$ redox reactions [4, 5]. Adjacent H_2-producing processes involve pyrolysis of plastic waste, paper and biomass, methane coupling into acetylene, dry methane reforming, hydrogen sulfide splitting and others.

TABLE 1. HYDROGEN MANUFACTURING COLOR CLASSIFICATIONS

H_2 color classification	H_2 manufacturing process	CO_2 emissions from plant operations, kg CO_2 per kg H_2 produced
Black	Bituminous coal gasification	18–20 [1]
Brown	Brown coal (lignite) gasification	7–14 [2]
Grey	SMR of natural gas	8–12 [1, 3]
Blue	SMR with CCS	0.4–6.5 [1, 3]
Turquoise	Natural gas decomposition	0–1.1
Green	Electrolysis of water using renewable energy	0

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Green hydrogen holds the key to a low-carbon future, but hurdles remain. Scaling production, creating compatible infrastructure, and ensuring safety are essential steps. Explore the path to sustainable energy.

This article discusses the thermodynamics, process configurations and technical challenges associated with turquoise hydrogen production. A companion piece to this article (see "Commercial Progress on Turquoise Hydrogen") covers the commercial development of turquoise H_2, along with the progress of companies and research organizations that are pushing the technology ahead.

At the present time, turquoise hydrogen is a competitor to incumbent grey hydrogen, produced by steam methane reforming (SMR), and to blue hydrogen, produced by SMR with added carbon capture and storage (SMR-CCS). Compared to SMR, methane pyrolysis consumes twice as much feed to produce the same quantity of hydrogen. However, it does not produce direct CO_2 emissions, and offers energy savings, as well as potential revenues from the sale of carbon co-product.

Methane pyrolysis

Methane can be viewed as a hydrogen carrier, like ammonia, rather than as a fuel. The methane pyrolysis (MP) reaction (Equation (1)), also called methane cracking, splitting or thermolysis, breaks methane molecules directly into elemental hydrogen and carbon at elevated temperatures, typically at 600–1,200°C:

$CH_4(g) \dashrightarrow 2H_2(g) + C(s)$ **(1)**
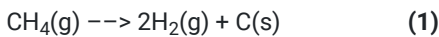
$\Delta_R H^0 = 74.85$ kJ/mol CH_4

$\Delta_R H^{1,000°C} = 91.7$ kJ/mol CH_4

The MP reaction is endothermic and requires 37.4 kJ/mol H_2 at standard conditions, in contrast to the 286 kJ/mol H_2 needed to produce green H_2 by water splitting through electrolysis or thermolysis. It also compares favorably to the 63 kJ/mol H_2 required by the SMR reaction combined with the water-gas shift reaction and steam generation for the reformer.

If all H_2 produced is combusted, the overall cycle can be viewed as burning off hydrogen only while leaving carbon intact. Combustion of produced H_2 yields 484 kJ/mol CH_4, which provides 60% of the low heating value of methane (802 kJ/mol CH_4), where carbon is fully oxidized to CO_2.

The MP process can thermally sustain itself since only 15–25% of available H_2 combustion heat is needed to provide the required heat for the reaction. The remaining 75–85% of H_2 produced can be exported or used onsite.

Methane conversion yield is promoted by low pressures and higher temperatures, in accordance with La Chatelier's principle. MP reactors are maintained above atmospheric pressure to prevent in-leakage of air anywhere in the process, to minimize reactor size and to speed the reaction.

As for kinetics, the reaction becomes spontaneous at approximately 550°C and attains chemical equilibrium at higher temperatures (1,300°C+) and higher pressures (>1 atm). Reaction rates at lower temperatures are relatively slow, so the overall conversion is kinetically limited. For this reason, considerable research efforts have been invested into developing catalysts capable of speeding up the reaction at lower temperatures.

For initial reactor sizing and determining the overall CH_4 conversion, the MP reaction rate, r, can be expressed through a simple first-order kinetic equation:

$r = -d[CH_4]/dt = k[CH_4]$ **(2)**

v   he reaction rate constant, k, is given by the Arrhenius equation.

$$k = \quad A \exp{(-E_a/RT)} \times [CH_4] \qquad \textbf{(3)}$$

The pre-exponential factor A and the activation energy E_a are determined experimentally and can be found in literature for specific reactor configurations. For example, Becker and others [6] present a compilation of A and E_a values for various reactor types.

Equation (1) does not account for reactive species, such as acetylene, ethylene, ethane and higher hydrocarbons, along with CO_2, H_2O and mercaptans that may be present in natural gas. To account for these species, schemes involving simultaneous reactions were developed.

A simple reaction mechanism for non-catalytic MP involving 5 reactions and 7 species was first proposed by Kassel in 1932 [32]:

$CH_4 => CH_2 + H_2$

$CH_2* + CH_4 => C_2H_4 + H_2$

$C_2H_6 => C_2H_4 + H_2$

$C_2H_4 => C_2H_2 + H_2$

$C_2H_2 => 2C + H_2$
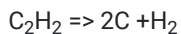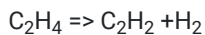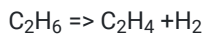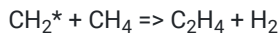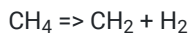
Currently employed MP reaction schemes involve a much larger number of reactions and species present to account for formation of higher hydrocarbons and polycyclic aromatic hydrocarbons (PAH) that are viewed as carbon precursors. For example, kinetic modeling of homogenous non-catalytic pyrolysis of methane and ethane performed by Younessi-Sinaki [33] used 242 elementary reactions and 75 species.

Other MP reaction mechanisms and kinetic models have been explored [7]. Molecular quantum mechanics (ab initio method) has been used to determine kinetic parameters for multiple reactions with many species [8]. Commercial software products for reactor modeling include general chemical process simulators, such as Aspen Plus or PRO/II, and specialized software packages developed for kinetic and equilibrium modeling of multiple simultaneous reactions occurring in high temperature gas mixtures, such as Chemical Workbench, CHEMKIN, PlasmaKin, or FactSage,. Commercially available CFD software packages, such as COMSOL Multiphysics, Ansys Fluent, and Open Foam, have also been used for MP reactor modeling.

Natural gas (NG), the main source of methane, is widely available through the existing 3-million-mile long pipeline infrastructure in the U.S., which is a significant plus for wide-ranging MP deployment. By contrast, transporting H_2 from centralized production facilities to potential users will require huge and challenging expansion of the existing 1,700 mile-long H_2 pipeline infrastructure.

The greenhouse gas emissions (GHGE) that originate within the MP plants include fugitive NG leaks and combustion of tail gas from H_2 purification operations. Offsite GHGE originate in upstream NG production, transport and storage operations, and involve NG leaks, flaring and combustion to generate heat for NG purification, power for pipeline compressors and associated fossil-fuel power plants. Operating plant emissions can be easily exceeded by offsite emissions, which stresses the importance of eliminating NG leaks everywhere in the supply chain, using power from renewable energy sources, or generating plant power onsite using H_2.

In the context of offsite impacts, it is worth noting that MP can remove CO_2 from the atmosphere if the feed is biomethane obtained by anaerobic decomposition of biomass, such as landfill gas, anaerobic digestor off-gas from green waste decomposition or from municipal and industrial wastewater treatment.

̲ction products

As stated above, the main products of the MP reaction are H_2 and solid carbon. The main uses of H_2 include:

• A reactant for production of basic chemicals (such as ammonia), petroleum refining, reduction of metal oxide ores, hydrogenation of fats and other processes

• A clean (no carbon emissions) fuel for processes requiring high-temperature heat, such as ore smelting, calcination, manufacture of cement, glass, ceramic materials and others

• A clean fuel for electric power generation and for propulsion of ships, locomotives and aircraft using either direct combustion or fuel cells. Automotive use is limited by lack of large-scale H_2 distribution infrastructure, although this can be changed by distributed modular MP systems

Produced elemental carbon can be used commercially as a filler for tire rubber and plastics, a pigment for ink and coatings, an adsorbent, a reducing reactant for pyrometallurgical applications, for electrodes manufacturing, and more recently, as a filament for production of structural polymers using carbon fibers, nanotubes (Figure 2) or graphene.
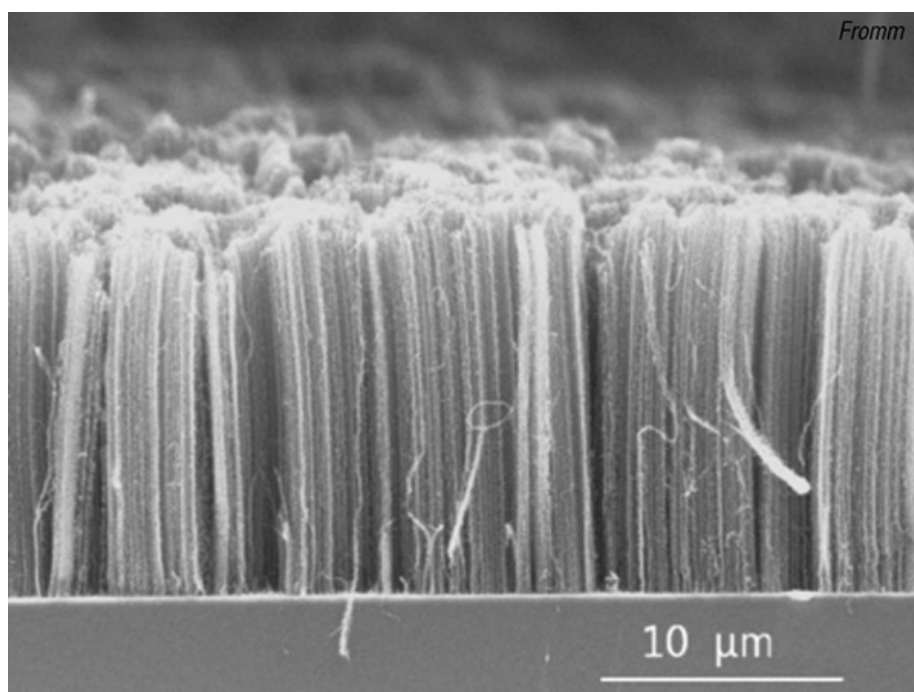

FIGURE 2. Methane pyrolysis processes can produce several forms of carbon, such as carbon nanotubes, like those shown here

If the MD process is deployed on a large scale commensurate with the current H_2 world-wide demand (around 97 million metric tons H_2/yr), the solid carbon produced (294 million m.t./yr of C) would far exceed current combined demand for carbon black, graphite, metallurgical coke, and anode coke (50 million m.t./yr of C). Unless new high-volume commercial uses are established, this huge excess of 244 million m.t./yr of C would have to be land-disposed (for example, in abandoned mines). This problem would be exacerbated if future demand for H_2 is increased — for example, replacing coke with H_2 in steel manufacture can increase H_2 demand by 90 million m.t./yr alone.

Perpetual storage of solid carbon does not pose the risk of CO_2 releases associated with CCS, which involves transporting and storing of liquefied or supercritical CO_2 under pressure in geological formations. Instead, the risks include carbon dust explosions and potential toxicity due to presence of residual carcinogenic polycyclic aromatic hydrocarbons (PAH). Fortunately, both of these risks c　　　mitigated. Unlike CO_2 pipelines required for CCS, transportation infrastructure for bulk solids is firmly in place. Also, filling empty mines with carbon could preserve some coal-mining jobs.

History of MP processes

Thermal decomposition of hydrocarbons has been known and practiced for well over a century with the first patent issued in 1891. Most applications have dealt with cracking of hydrocarbons in petroleum refining to produce smaller and more useful molecules. Past commercial applications of MP were limited to production of acetylene and of carbon black using Hüls process based on thermal plasma arc reactor [30].

In the second half of 20th century, MP was commercially employed in 1989 to produce commercial carbon black and hydrogen as a byproduct [31]. This thermal plasma arc process was developed jointly by Kvaerner and SINTEF starting with 150 kW test reactor in Trondheim, Norway, followed by 3-MW pilot plant in Bofors, Sweden that led to commercial size Karbomont plant near Montreal, Canada. The plant started operations in 1998 but closed down in 2002 because of financial difficulties and technical problems.

The Kvaerner/SINTEF technology for non-metallurgical applications was subsequently acquired and improved by Monolith Materials, a U.S. company, who is currently the only commercial producer of carbon black and hydrogen via MP in the world. The undergoing expansion of their Olive Creek operating facility in Hallam, NE will result in the plant capable of producing 180,000 m.t./yr of carbon black and 60,000 mt/yr of H_2, most of which will be used to produce 290,000 m.t./yr of anhydrous ammonia onsite.

In recent decades, MP has garnered a lot of attention because of its promise to decarbonize hydrogen production in a cost-effective and energy-efficient way. In addition to thermal plasma reactors, several other routes have been identified and are in different stages of development.

Process configuration

The block flow diagram shown in Figure 1 shows a generic MD process and outlines various technology alternatives. Brief descriptions of the process steps follow.
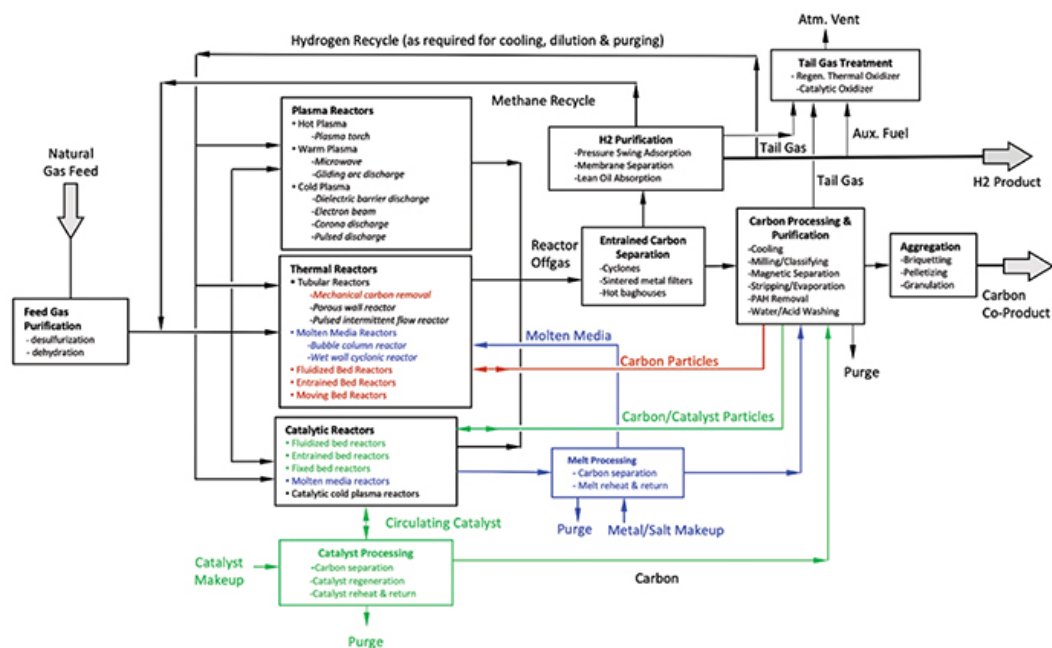
FIGURE 1. This flow diagram shows the elements of a generic methane-pyrolysis process used in manufacturing turquoise hydrogen

Feed purification. Pipeline-quality natural gas feed may be treated with zinc oxide (ZnO) to remove odorant mercaptans and any residual H_2S prior to reaction to avoid metal catalyst poisoning. For thermal or carbon-catalyzed reactors, the desulfurization step is not necessary, since minor amounts of H_2S and mercaptans in the feed actually promote methane decomposition in the presence of

carbon [7]. In general, small concentrations of C_2 to C_{6+} hydrocarbons, CO_2, N_2 and H_2O should not significantly affect the methane pyrolysis process, although their process fate, such as methane-water reactions leading to CO or CO_2 formation, needs to be considered in the overall process design. One concern arises if C_{2+} hydrocarbons are present in NG at higher concentrations, which could lead to excessive carbon deposition. Mitigation measures may include pre-pyrolysis reactors [8].

Methane pyrolysis reactors. Methane pyrolysis reactors can be grouped into three categories: plasma, thermal and catalytic. Table 2 contains descriptions of each reactor type.

TABLE 2. METHANE PYROLYSIS REACTOR TYPES	
Reactor type	**Description**
Plasma reactors	Plasma reactors consist of both thermal (hot) plasma and non-thermal plasma reactors. In hot plasma reactors, the feed gas is heated to high temperatures (<2,000°C) by an electric arc inside a plasma torch either directly or by mixing it with hot (<6,000°C) plasma gas generated by passing H_2 through a plasma torch. Methane chemical bonds are broken by thermal vibration and excitation. Plasma gas is mixed with part of the incoming feed and routed to the reaction chamber, where it is mixed in stages with the remaining feed gas. The reaction chamber provides residence time for recombination of formed free radicals and ions into final reaction products. In non-thermal plasma reactors, the feed gas is typically heated to 700–900°C by passing it directly through either "warm" plasma (1,000–6,000°C) generated by microwaves or by gliding arc discharge, or "cold" plasma generated by dielectric barrier discharge, electron beam, pulsed discharge or corona discharge. In non-thermal plasma reactors, C-H bond breakup is aided by interactions with high-energy (high-temperature) electrons. Methane conversion and reaction product composition depend on plasma generator type.
Thermal reactors	Thermal reactors typically operate at 1,000 to 1,200°C to provide acceptably fast thermal and mainly non-catalytic CH_4 decomposition using the following configurations: •Tubular reactors, where flowing gas mixture is heated by reactor walls that are kept hot by external heaters or hot fluegas from H_2 combustion •Fluidized-bed reactors where reactions occur both in the reacting gas mixture and on the surface of fluidized particles. Typical configurations employ bubbling beds where most of the gas is contained in the bubbles rising through dispersed particle (emulsion) phase. The heat is delivered by hot reactor wall or by a side stream of solid particles circulated through an external heater •Entrained-bed reactors (also known as fast bed, spouted bed or riser reactors) employ a lift tube (riser) inside which the reacting gas mixture and entrained particles rise together and empty into a separation chamber. De-entrained particles descend in the annulus surrounding the lift tube to be removed at the reactor bottom. Some fraction of particles is recycled back to the lift tube before removal •Moving-bed reactors where a downward-moving dense bed of particles is in direct contact with an upward-moving gas. External induction coils heat the reactor wall around the reaction zone, although other heating methods can also be used •Molten-media reactors where a reacting gas mixture is bubbled through a pool of molten metal or salt (or both) heated by electric immersion heaters, by hot reactor wall, or by an external melt circulation heater. Configurations include (a) bubble column reactors where carbon formed inside the rising gas bubbles accumulates on top of the melt and is removed through an overflow, (b) wet-wall cyclonic reactors where the descending rotating melt film removes carbon from the reactor, and (c) capillary slug-flow reactors
Catalytic reactors	Catalytic reactors use a catalyst to accelerate MP reactions, promote CH_4 conversion at lower temperatures (<1,000°C), and improve selectivity toward H_2 and/or toward the desired form of carbon. Catalytic reactions can be conducted in tubular reactors, fluidized bed reactors, or in molten media reactors

Entrained carbon separation. Carbon particles entrained in the reactor exit gas can be separated using cyclones, sintered-metal filters or high-temperature baghouses equipped with ceramic filter elements.

H_2 purification. In this step, H_2 is separated from unreacted CH_4, C_{2+} hydrocarbons and other species present in the filtered and cooled reactor offgas. The separated hydrocarbon-rich stream is recycled back to the reactor. Separation processes include pressure-swing adsorption (PSA), membrane separation and lean oil absorption/desorption. These processes can also be used to remove non-hydrocarbon species (such as N_2, CO_2, H_2S and H_2O) from the reactor offgas. To prevent their buildup, the hydrocarbon-rich recycle stream must be purged, or a separate stream containing these compounds would have to be generated (for example, through staged PSA depressurization and purge sequence).

A portion of the purified H_2 may be recycled back to the process for plasma-gas generation and/or cooling, heating, dilution or purging needed to minimize carbon deposits on feed-gas injection nozzles or reactor walls.

Tailgas treatment. Since the purge or the tailgas may include small amounts of hydrocarbons, CO, or H_2S, direct atmospheric discharge may not be acceptable without treatment using either regenerative or recuperative/catalytic oxidizers. To minimize carbon footprint, high energy efficiency is required, and produced H_2 should be considered for auxiliary fuel.

Carbon processing and purification. Separated carbon that exits the reactor, cyclone, or filter as a dense particulate stream may require cooling prior to subsequent steps. This can be performed in bulk solids coolers employing vertical plate or tube coil exchangers, rotary coolers or jacketed augers.

Size reduction using high-velocity gas jets, micro-pulverizers, or continuous ball, rod or pebble mills, along with the particle size classifier and recycle may be necessary to produce particles suitable for recirculation back to a fluid-bed or to a moving-bed reactor after reheating.

Carbon co-product may have to be stripped of adsorbed H_2, H_2S, CH_4 and larger hydrocarbons to alleviate safety concerns in downstream handling. Stripping may be performed using steam-blown or air-blown rotary drums or fluid beds. If reducing residual PAH concentrations is desired, carbon can be heated to high temperatures to volatilize and/or pyrolyze PAH while stripping lighter species. Alternatively, PAH may be removed using solvent extraction [9] and possibly recycled back to the MP reactor. Stripper off-gas should be routed to the tailgas treatment before atmospheric venting.

Carbon particles removed from molten media reactors may be contaminated with salts or metals, which can be removed by evaporation in a rotary kiln or in a tunnel furnace. Water-soluble salts may be removed by a water washing cascade with an evaporator/crystallizer to recover the salts, and a dryer to dry washed carbon product. Metal contamination may also be removed by particle-size classification, magnetic separation or acid washing.

Carbon aggregation. In this step, fine carbon particles are aggregated to mitigate dusting from subsequent solids-handling operations and the associated safety and environmental concerns. Particle size can be increased through briquetting, extrusion granulation or pelletizing after addition of suitable binders. Other steps may be required for carbon nanomaterials.

Melt processing. This step is needed for molten-media reactors to remove any carbon and impurities present in the melt to prevent their accumulation to unacceptable levels. While carbon can be removed by melt filtration, dissolved contaminants may require purging, which necessitates makeup or periodic replacement. Purged molten metal can be solidified and recycled offsite. Purged salt may have to be disposed of as process waste. A melt circulation loop with a reheater and electromagnetic pump can be used as a heat carrier, although heating coils placed inside the reactor can also provide this function.

Catalyst processing. Catalyst mixed with carbon is withdrawn from fluidized- or moving-bed reactors as a dense particle stream. Processing may entail milling followed by separation of carbon and catalyst through sieves or particle-size classifiers. It also can include catalyst regeneration, whereby carbon deposits are burned off or gasified using steam, and catalyst reheating prior to

recycling back to the reactor. Catalyst purge and makeup are also performed at this step. Molten-media catalysts require purification, purge and makeup (see melt processing). The recirculating catalyst stream can be reheated before returning to the reactor to serve as reaction heat carrier.

Technical challenges

The MP process poses technical challenges. Four of the main ones — carbon deposition, slow reaction, delivering heat to the reactor and heat recovery — are discussed below.

Carbon deposition. Carbon deposition on internal surfaces of tubular reactors leads to reactor plugging and unstable operation. Fouled reactors must be periodically shut down to remove carbon deposits from the walls and feed-gas injectors, and replacing or regenerating the fixed bed of catalyst. This necessitates the use of multiple parallel reactors to maintain production continuity, which adds cost and considerable complexity to the process.

Mitigation approaches include the use of a wet-wall reactor, where the internal reactor surface is wetted by a rotating or falling film of liquid metal or salt [10], a porous-wall reactor (in the context of methane chlorination leading to hydrogen and carbon) [4], or using less adherent surfaces, such as calcium-oxide wall coating to facilitate mechanical carbon-deposit removal [11] or ceramics, including alumina, MgO-C, or SiC [8].

Carbon buildup in plasma torches was addressed by the company HiiROC (Hull, U.K.; www.hiiroc.com) by using H_2-purged porous anodes in combination with vortex flow inside the torch chamber [12].

Ekona Power Inc. (Burnaby, B.C.; www.ekonapower.com) developed a pulsed intermittent-flow reactor where carbon deposition is mitigated by strong turbulence associated with rapid depressurization and high-velocity gas flow [13]. Nonrecoverable ferrocene $Fe(C_5H_5)_2$ and sulfur adjuvants have been used to promote carbon nanotube formation without carbon wall deposits in a downflow tubular reactor tested by Huntsman (The Woodlands, Tex.; www.huntsman.com) for production of Miralon, a carbon nanotube material [14, 15].

Prevention of carbon buildup led to the development of fluidized-bed reactors, moving-bed reactors and bubble-column reactors, all of which are being actively pursued by commercial firms. In the fluidized-bed reactors, carbon preferentially forms on the surface of fluidized particles which grow in size and are continuously removed from the bed by gravity-settling below the gas distributor or using an internal overflow weir near the top of the bubbling fluid bed, as in the process developed by Pacific Northwest National Laboratory (PNNL; Richland, Wash.; www.pnnl.gov) that uses fluidized iron-based catalyst [16].

Alternatively, fluidized catalyst particles can undergo attrition and phase transformation inside the bed, releasing accumulated carbon in the form of fine particles that are entrained into reactor gas and then elutriated out of reactor, as is done in the Hazer Group Ltd. (Perth, Australia; www.hazergroup.com.au) process that uses iron ore catalyst in multistage fluidized-bed reactors [17].

In the moving-bed reactor being developed by BASF SE (Ludwigshafen, Germany; www.basf.de) [18], a dense phase of carbon particles moves downward countercurrent to the gas flow inside a cylinder equipped with the hot wall reaction section heated by external induction-coil. Hot solid carbon particles exchange the heat directly with the reacting gas moving upward. Carbon particles grow due to deposition of formed carbon on their surface which, along with the wall shear forces, prevents carbon deposit on the reactor walls.

Bubble-column reactors mitigate carbon deposition, as the reactions take place inside gas bubbles rising through a pool of molten ɾ   such as metals (Sn, Pb, Ga, Te, Ni-Bi, Cu-Bi, Ga-In-Sn) or salt (KBr, NaBr, NaBr/KBr, NaF, KCl, NaCl, $MnCl_2$), acting as heat

transfer fluids at 900–1,400°C and often as catalysts. Molten media is contained inside a cylindrical reactor that may be provided with a submerged packed bed of ceramic rings or sprays in the vapor space to increase liquid-gas interface. Carbon wall deposits are mitigated by carbon formation at the bubble-liquid interface, which keeps it contained inside the bubble. When rising gas bubbles burst upon reaching liquid surface, carbon is released and floats on the melt surface, from where it can be continuously removed using an overflow weir or gas flushing.

Hydrocarbons (mainly C_2H_4 and C_2H_6) may be present at <2% molar concentration in the reactor off-gas. Higher hydrogen yields are promoted by catalytic molten media (such as Ni-Bi), higher liquid temperatures and longer residence times. Challenges include carryover of molten media vapor and its subsequent condensation and freezing outside of reactor. Resultant plugging can be mitigated by quenching the off-gas with cold H_2 inside the reactor. Also, salt or metal contamination of carbon is often a problem which requires carbon purification steps involving high temperature evaporation or washing using water or acid.

Other issues include melt stability, large reactor size due to high gas residence times, and high corrosivity of molten salts. Purging gas injectors/distributors with inert gas or H_2 may be required when NG feed is interrupted to avoid liquid metal or salt from getting inside the injectors and solidifying. Use of ceramics, special alloys, or lined vessels is necessary to counter corrosivity of molten salts or metals.

Slow reaction. As discussed above, the methane pyrolysis reaction is relatively slow. While raising the reaction temperature helps, when temperatures exceed 1,300°C, the equilibrium yield of H_2 starts to decrease due to the formation of acetylene, ethylene and ethane. Moreover, higher temperatures result in higher net energy consumption. To lessen the residence time and the reactor volume, it is possible to increase reactor pressure, but at the expense of H_2 yield. For these reasons, reactor design must carefully examine H_2 yields and exit gas compositions as a function of reaction temperature and pressure along with staged feed-gas injection and staged dilution/cooling with H_2. Multiple competing reactor configurations need to be analyzed using kinetic modeling to optimize the reactor design.

Various catalysts have been developed to accelerate MP reactions at lower temperatures (<1,000°C) and to improve selectivity toward H_2 and desired allotropic form of carbon; these include the following:

• Solid catalysts, such as metals (Co, Fe, Ni, Si), metals/alloys with promoters/dopants (Ni-Cu, Ni-Pd, Ni-Mo, Ni-La, Ni-Cu-Co, Ni-Sn, Fe-Co, Fe-Mo, Zn-Cu) supported on silica, alumina or carbonaceous materials, metal oxides (FeO/Fe_2O_3, La_2NiO_4), metal carbides ($Fe_3 C$, $Ni_3 C$), and metal-carbon nanostructures (Ni-C)

• Molten-media catalysts, such as liquid metals (Te, Ni-Bi, Ga, Pb), liquid salts (NaCl, KCl, $MnCl_2$, $NiCl_2$, NaBr, KBr, Na_2CO_3, K_2CO_3, Li_2CO_3, or their mixtures), liquid salts with dispersed solid catalyst particles in the form of finely divided elemental metals (Ni, Mo, Mn, Co, Fe, Zn, Ti, Cu), their oxides, carbides or their mixtures, and carbon catalysts (activated carbon, carbon black, graphite and formed carbon). A recent comprehensive review of MP catalysts was conducted by McConachie [8].

Relative to solid catalysts, molten-media catalysts are not prone to carbon buildup. However, their stability is affected by high temperature. Metal catalysts' activity depends on the metal (Ni>Co>Fe) and exceeds that of carbon catalysts [7]. Rapid solid catalyst deactivation caused by carbon buildup, poisoning and sintering is the key concern. Susceptibility to deactivation is higher for Ni-based catalysts than for Fe-based and carbon-based catalysts.

Conventional reactivation of solid metallic catalysts removes carbon deposits using oxidation or steam gasification, and results in CO_2 emissions. This is avoided in the process developed by PNNL, where bimetallic Ni-Cu catalyst on a carbon nanotube support is υ   pyrolyze methane at 600°C inside a fluidized bubbling-bed reactor [16]. Formed carbon accumulates on catalyst particles, which are withdrawn from the bed, cooled and acid-washed to separate formed carbon from metallic catalyst precursors. Catalyst

precursors are then used to resynthesize the catalyst for recycle back to the reactor. The catalyst can be formulated to increase selectivity toward formation of carbon nanotubes.

Iron-based solid catalysts are more stable and deactivate at slower rates than Ni-based catalysts. The process developed by Hazer Group uses fluidized iron ore (Fe_2O_3/FeO) catalyst particles [*17*]. Carbon forms as graphite on the surface of catalyst particles, which undergo continuous attrition through intergranular breakup, releasing small graphite particles into the reactor offgas. Catalyst surface is thus continuously regenerated, preventing deactivation due to carbon buildup. Separation of elutriated solid catalyst from carbon is one of the challenges in such systems.

As previously mentioned, special once-through non-recoverable "catalysts" have been used to promote carbon nanotube formation in tubular MP reactors. These include ferrocene $Fe(C_5H_5)_2$ and sulfur additives. Use of ferrocene and iron pentacarbonyl $Fe(CO)_5$ was investigated for the production of hydrogen in solar-heated reactors [*28*].

Carbon catalysts are considerably less expensive, but also are less active than metallic catalysts, leading to higher operating temperatures (800–1,000°C) and longer residence times to achieve equivalent conversion. Amorphous carbons (carbon black, activated carbon) are more active than ordered forms, such as graphite. Advantages for carbon catalysts over metallic catalysts include negligible toxicity, high stability, longer lifetimes and no susceptibility to sulfur poisoning, which makes desulfurization of the natural gas feed unnecessary.

Regeneration of carbon catalysts may be performed through gasification with steam, which generates CO_2 and H_2. However, this is not needed for the once-through use of imported carbon catalyst with higher activity, such as activated carbon. Also, it may be preferable to rely on autocatalytic properties of formed carbon product instead of a once-through use of imported catalytic carbon, as practiced by Modern Hydrogen Inc. (Bothell, Wash.; www.modernhydrogen.com).

Low catalytic activity of formed carbon can be compensated for by increasing the circulation rate of carbon product through the reactor, which increases the exposed particle surface area within the reactor.

Methane decomposition can also be achieved through photolysis using heterogenous photocatalysts inside fixed-bed tubular reactors with transparent walls illuminated by external light.

Delivery of heat to the reactor. In addition to the enthalpy required by the endothermic MP reaction, sensible heat is needed to get the reactants to the desired temperature. The overall reaction heat requirement depends on the size of the recycle streams, and can amount to 1.2–1.5 times the reaction endotherm.

In plasma reactors, the heat requirement is provided by electricity powering a plasma generator. Hydrogen or staged feed-gas injection can be used to control the temperature profile. No additional heat source is required.

In non-plasma small-scale experimental reactors, heat is typically delivered to the reacting mixture through a hot reactor wall, whereby the reactor is placed inside an electric furnace or heated using external resistors or induction coils. Such a scheme does not scale up well with growing reactor diameter, because the radial temperature gradient becomes very steep and efficient heat transfer becomes more difficult.

To circumvent scaleup issues associated with externally heated reactors, pilot- and demonstration-scale plant design should consider a circulating side-stream of molten metal or salt, carbon particles or catalyst particles, as a heat carrier. Circulating stream(s) would be withdrawn from the reactor, processed as necessary, reheated and recycled back. External reheaters can utilize resistive, induction

and microwave heating, electric arc furnace, H_2 -burning fired heaters, concentrated solar heating or immersed plasma torch (molten media only).

One example of MP reactor heating is shown in Figure 4, where molten salt floating on top of a molten Ni-Bi catalyst pool is circulated through an external-fired heater before returning to the bubble-column reactor.
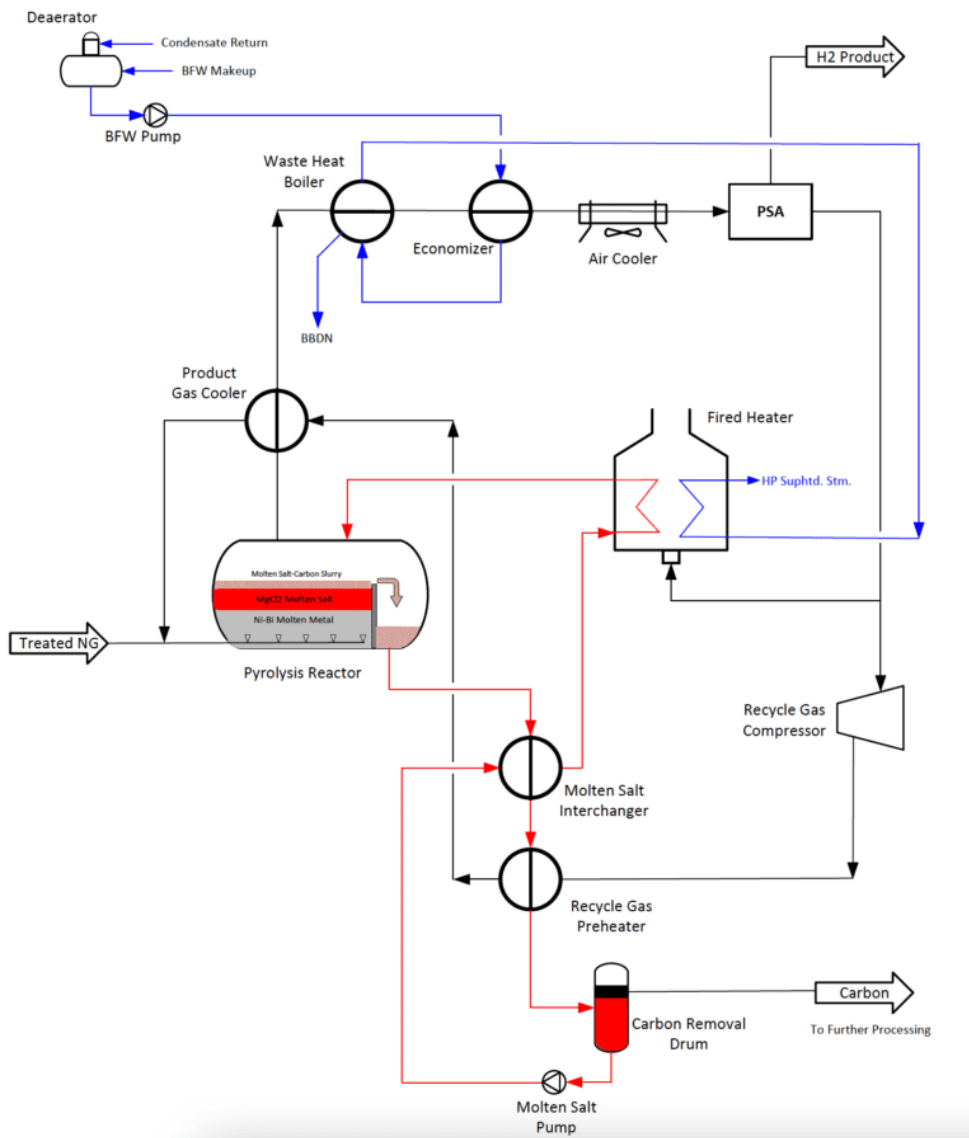

Figure 4. Heating of bubble-column reactor using forced circulation of molten salt (adapted from Parkinson et al. [25]

Using combustion heat to provide MP endotherm was explored by Muradov [27], whereby a small amount of oxygen is added to a fluidized-bed catalytic reactor employing carbon and iron-based catalyst. Emissions of CO_2 would still be 3−5 times smaller compared to the conventional SMR process. A similar approach is used by C-Zero, whereby H_2 is combusted to heat a circulating molten media inside a bubble column reactor.

Other schemes of delivering heat to reactors are being researched. One of them under development by Palo Alto Research Center [19] involves condensation of zinc vapor to supply the reaction heat inside a molten zinc cyclone reactor. A scheme proposed by Munera-Parra [20] uses chemical energy obtained through exothermic recombination of molecular hydrogen from plasma-generated atomic hydrogen. A novel method utilizes compression heating of methane to pyrolysis temperature using a supersonic shock wave g   :ed by wave rotor reformer technology [21]. Microwave heating of fluidized bed was patented by H-Quest [22].

Heat recovery. The overall heat requirement can be significantly reduced by using heat recovery from reactor outlet streams, or by utilizing waste heat from adjacent processes (for example, from cooling of steel and slag in steel production served by dedicated MP installations) [29].

Heat can be recovered by preheating the feed stream (natural gas mixed with methane recycle) and H_2 recycle stream against the reactor exit streams. Caution must be exercised to avoid coking inside heat exchanger tubes due to overheating of the feed stream.

Owing to the high heat capacity of H_2, most of the heat leaving the MP reactor (~80%) is carried by the gas with the remaining 20% carried by carbon. The entire reactor offgas stream can be sent through a shell-and-tube heat exchanger prior to the solids separation step, as practiced in some carbon black plants. Alternatively, hot carbon is separated in a cyclone or inside the reactor, prior to heat recovery from the solids-free gas through steam superheating, followed by steam generation, and followed by an economizer. Heat can be recovered from carbon using a bulk solids cooler equipped with a vertical plate or coil-tube exchanger.

Superheated steam can be utilized in a combined-cycle cogeneration system employing H_2-fueled gas turbine to generate power for the plant, as well as for export. Such a system would also provide operational flexibility to accommodate swings in external H_2 demand.

For more information, see the complementary article, "Commercial Progress of Turquoise Hydrogen".

MP process economics

Publications dealing with techno-economic analysis of MP technologies use a wide-ranging set of assumptions, methodologies, plant capacities and unit pricing of natural gas, carbon, electricity, water, consumables, labor, carbon-offset credits and other parameters. Because of this variability, the published data do not allow for equitable comparison of projected economic performance of competing technologies. Nevertheless, reviewed articles provide valuable insights into expected economic performance of methane pyrolysis technology and are summarized as follows (for uniformity, all costs are expressed in 3Q 2023 dollars):

• Hydrogen production costs using SMR-CCS technology varied from $1.40/kg to $2.50/kg of H_2, depending on natural gas cost and other factors used in analysis [23, 24, 16]

• For molten salt (KCl-MnCl$_2$) bubble-column reactors, projected H_2 production cost is $1.80/kg of H_2 based on natural gas at $2.30/GJ and zero revenue for produced carbon [24].

• Hydrogen from molten media (Ni-Bi metal and salt) reactors costs $1.70/kg of H_2 to produce, which is much less than water electrolysis based on polymer electrode membrane (PEM) technology ($3.00/kg H_2 for electricity cost alone). A carbon-offset credit of $26/ton CO_2 is required to achieve cost parity with SMR. Alternatively, carbon co-product revenues would have to exceed $200/ton carbon for the same effect [25].

• For fluidized-bed reactors using solid Fe-based catalysts, projected H_2 production cost was $3.20−3.50/kg H_2 based on natural gas at $7.50/GJ, with zero revenue for produced carbon, and no catalyst recycle or carbon purification, all against $2.50/kg H_2 for SMR-CCS benchmark. For H_2 to become competitive with SMR-CCS, 20% of produced carbon would have to sell at $1.20−1.50/kg. The economics and thermal efficiency are highly sensitive to catalyst activity and resulting H_2 yield [15].

• Carbon co-product revenue in the $600−900/ton range will completely offset H_2 production cost [26].

• The H_2 production cost from a fluidized-bed MP reactor will match that of an SMR process (without CCS) if carbon sells for $300−
8   า [27].

• Production cost of H_2 from the MP process based on a hot cyclone reactor wetted by liquid Zn metal is \$2.50/kg of crude (94%) H_2, and \$3.40/kg pure (99%+) H_2 with zero carbon revenues for both cases [19].

Overall, turquoise H_2 can be produced at \$1.80−4.00/kg without carbon sales or offsets, which is not yet cost-competitive with grey H_2 (\$0.90−3.00/kg to produce). However, turquoise H_2 may compete favorably with blue hydrogen produced at \$1.40−2.50/kg by SMR-CCS.

The economic feasibility of turquoise hydrogen can be vastly improved by selling carbon co-product and generating revenue from carbon-offset credits or from avoided carbon tax (for example, obtained by replacing SMR or oil-derived carbon black plants with an MP process).

Economic feasibility can also be improved through technical innovation. For example, the ETCH process [5] that employs Ni-based redox reactions is projected to produce H_2 at \$1.00−1.50/kg of H_2 without carbon sales or carbon offsets revenue, which compares favorably to SMR.

Current growing demand for carbon black and graphite creates significant market opportunities for MP-produced carbon. However, new markets for carbon are needed to strengthen the driving force required for broad adoption of MP technology.

Large-scale grassroots MP plants will have to compete with fully amortized existing H_2 plants. For this reason, it may be worthwhile to consider the feasibility of retrofitting the existing installations with MP reactors and solids handling subsystems.

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