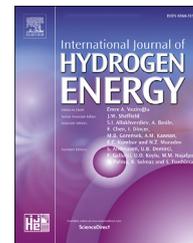




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High temperature production of hydrogen: Assessment of non-renewable resources technologies and emerging trends

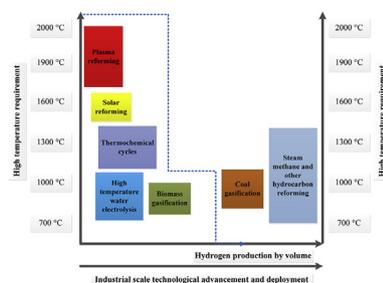
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HIGHLIGHTS

- Wide range of hydrogen utilizations are key drivers to its increasing demand.
- Fossil based hydrogen production continues to play dominant role in the hydrogen economy.
- By production volume and technological advancement, reforming of natural gas takes the lead.
- Non-renewable resources benefitions via high temperature processes were discussed.
- Emerging developments in industrial scale reforming with renewable solutions were assessed.

GRAPHICAL ABSTRACT



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ABSTRACT

Conventional productions of large volume of hydrogen from fossil based resources continue to play a key role in the hydrogen economy. This paper recalls the contribution of these conventional technologies with new technological development and researches. Providing gradual integration of renewable solutions into large-scale production, some emerging developments in the use of the renewable based feedstock and energy resources in reforming processes in order to bridge the gaps from conventional use of fossil feedstock to improve various conversion processes were discussed. This paper focuses on high temperature process technologies for producing hydrogen via non-renewable resources and various industrial technologies and processes (700 °C and above) for the beneficiation of the available carbonaceous feedstocks like natural gas, other hydrocarbons (other fossil based options), coal etc. The paper concludes with the analysis of some development gaps in hydrogen production from various resources, which interplays between the renewable

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Hydrogen economy
Gasification

and non-renewable resources as well as likely future trends that should be expected in the hydrogen market in the next decades.

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Introduction

Recent increase in the use of hydrogen in sectors like energy, chemicals production, transportation and manufacturing industries have necessitated more efforts in experimental research, technological development and political interests across the globe. These efforts are geared towards finding alternatives to producing sustainable clean hydrogen from the abundant resources available around the world. The steam reforming of natural gas and gasification of coal have been the most dominant technologies for producing huge volumes of hydrogen at industrial scales. As the most abundant element in the universe, hydrogen is without exception an energy carrier and clean fuel to tackle environmental challenges and concerns resulting from fossil fuel usage [1,2]. The dependence of economic growth on fossil based resources by industrial processes and the transportation industry continues to increase across all continents so as the demand for hydrogen. The wide application of hydrogen in many industrial processes for the manufacturing of commodity chemicals and fuels as well as its production from wide range of primary feedstocks and/or materials resources makes hydrogen to play a crucial role in energy transition and energy security [3]. Well-known technological processes like thermolysis, electrolysis, photolysis (e.g. photocatalytical, photobiological and photoelectrochemical processes) and thermochemical conversions are all applied to transform feedstocks into hydrogen and other side products [4]. These processes require heat and sometimes catalysts to initiate chemical reactions that results into the production of hydrogen.

Globally, fossil based hydrogen production has been the most common technique used until today and the largest use of hydrogen is in industry and refining processes, where hydrogen originates as a by-product of industrial process plants as well as major product from reforming of hydrocarbons and coal gasification [1,5–8]. In addition, major drivers for hydrogen market growth and its use for processing in the petroleum industry are: stringent regulation on deep desulfurization of transportation fuels, high growth in transport fuel demands and sweet-sour crude oil quality and imbalance, sour natural gas amongst others. According to the IHS Markit's Chemical Economics Handbook, Fig. 1 shows the world consumption of hydrogen for the year 2017 with China leading the chart due to stricter fuel sulfur policy in order to lower the high level of urban pollution, the Middle East demand more hydrogen to process huge production of sour natural gas, followed by United State as their lower natural gas price favor the increase in ammonia production market.

As a confirmation to the world's dependence on fossil based resources, over 85% of the world primary energy for 1995 and 2017 originates from fossil based routes. Fig. 2 shows

the percentage of the world's total energy consumption by source for 1995 and 2017 with the forecast by the year 2040 (predicted values) [9].

Hydrogen production growth is expected to increase at a robust rate due to its demands and wide applications. The Power-to-Gas (PtG) process concepts have provided alternative routes in the storage of electric energy in form of hydrogen, which is critical to the excess renewable energy production and energy transition [10,11]. Besides the over 85% usage of hydrocarbons as the major world's energy sources for the year 1995 and 2017 in Fig. 2, the profile also illustrates the projected changes in the energy mix by 2040 as the renewable energy resources are expected to deliver electricity, hydrogen and other carbon neutral fuels and chemicals.

Although, the nuclear hydrogen production is promising with the zero carbon sources it offers. Nuclear power plants are provider of high-temperature heat that is applicable for hydrogen production via electrolysis. Factors influencing the nuclear power technology attractiveness range from: increase in fossil fuel (coal, crude oil and natural gas) production rates and prices, government policy and regulation on greenhouse gas emissions by source, safety concerns and others. In the future, the application of various renewable energy sources is expected to increase significantly (according to Fig. 2). The choice of any hydrogen production techniques depends on the favorable geo-economics potentials that support its production, cost of primary energy resources, energy policy strategy, advancement and performance of the hydrogen technological infrastructure components [12]. This work recalls and focuses on technological options and assessment of various high temperature hydrogen production techniques that are already implemented for industrial scale with emphasis on major fossil based feedstocks and different energy sources. These technologies are regarded as conventional and highly advanced. The current trends in the reforming and gasification technologies are discussed and how these techniques will continue to play significant role in the hydrogen economy.

Non-renewable feedstocks and energy sources for hydrogen production

Crude oil, coal and natural gas are energy resources and organic chemical feedstocks for the production of hydrogen. Fig. 3(a) and (b) illustrate the feedstocks and the energy sources for production of hydrogen respectively. The energy can be provided in the form of electricity during process operations to power process units or heat to enable process heat in reactors, which could support either endothermic or exothermic reactions during thermochemical decomposition or formation. Non-renewable feedstocks are available in form of gas (natural gas), liquid (crude oil), solid phase (heavy oil

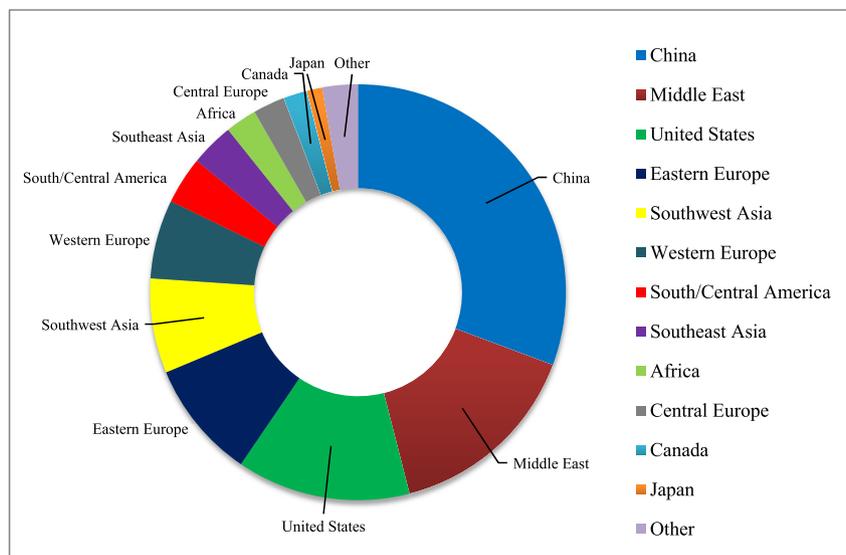


Fig. 1 – 2017 world consumption of hydrogen according to IHS Markit's 2019 Chemical Economics Handbook report on Hydrogen.

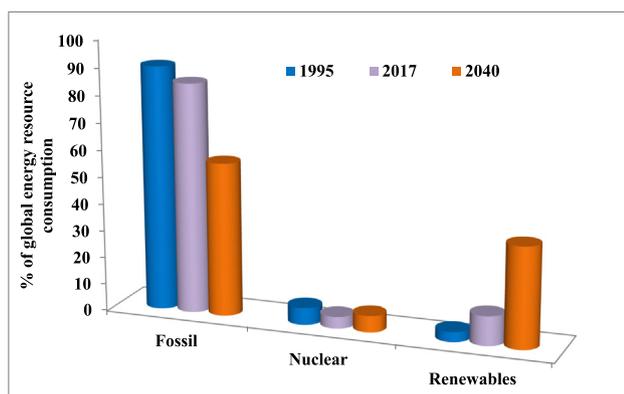


Fig. 2 – World's percentage of energy consumption by source for the year 1995 and 2017 with forecast for the year 2040.

residues, bitumen, coal, etc.), and their processing and utilization can be fueled with energy provided by any of the energy sources (heat or electricity). These feedstocks thermochemical conversion shall be discussed in section [Fossil fuel hydrogen production technologies](#) in order to evaluate the technological pathways for fossil based or non-renewable resources production of hydrogen.

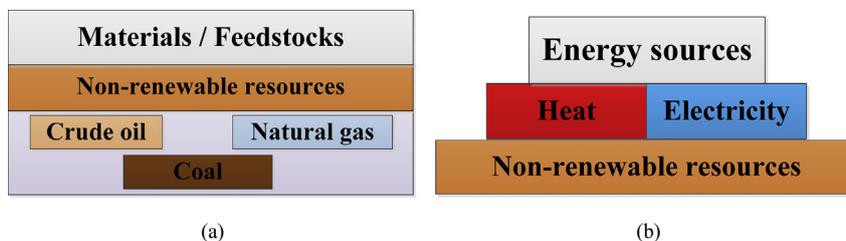


Fig. 3 – (a) Some fossil based feedstocks for hydrogen production. (b) Energy sources from non-renewable resources for hydrogen production.

Fossil fuel hydrogen production technologies

Over several decades, the most widespread hydrogen production has been from extensive utilization of fossil resources, although, the evolution of each technology differs with its own peculiar process chain(s) and feedstocks, these technologies have contribute to the beneficiation of carbonaceous resources apart from their harmful emissions like oxides of carbon, nitrogen, sulfur, environmental impact and global warming potentials [13]. This section shall recall a wide range of industrial hydrogen production technologies, more detailed processes with their operational parameters and discuss some of the emerging developments.

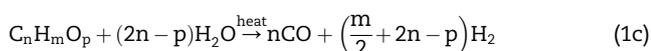
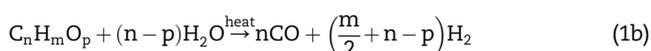
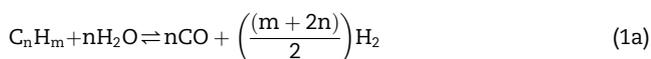
Reforming processes

On commercial scale, reforming processes have been the most dominant of all the high temperature processes to produce hydrogen from varieties of fossil resources, over 90% was produced through reforming of natural gas with steam in the last decades [14]. Other feedstocks could be any of gaseous, liquid hydrocarbons and alcohols or sometimes carbohydrate [2,6]. Reforming processes provides alternative pathways for obtaining industrial scale hydrogen due to the efficient utilization of the raw feedstocks and industrial maturity level of

the processes. Though there are many process options in this category. The following sub-sections shall recall and discuss the technological perspectives of each production scheme.

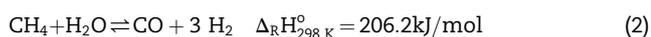
Steam reforming of hydrocarbons

Steam reforming of any hydrocarbon involves highly endothermic conversion of such hydrocarbon and water vapor or steam into hydrogen and carbon monoxide in a catalytic tube reactors, which is also known as reformer. Depending on the reactor design, the hydrocarbon feedstock maybe preheated before it is fed into the reactor with any of the following overall reactions (1a, 1b and 1c) [2]:



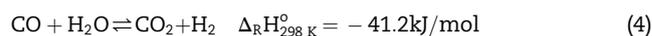
It important to note that the process efficiency of steam reforming largely depend on some factors such as reactor configuration, the nature of applied catalyst, the selectivity of the membranes for further purification of product gas, the process parameters and variables like temperature, pressure and reactor volume [8,15,16]. The endothermic reaction implies that it requires heat supply to the process from external firing or direct-flame-heat [2,16]. These reactions (1a, 1b and 1c) can be further summarized into series of chemical reactions with example of typical hydrocarbon like methane (CH₄), liquid hydrocarbons as well as alcohols.

(a) *Steam methane reforming.* Commercially, steam methane reforming (SMR) is the most extensive method to produce hydrogen with conversion efficiency in the range of 74–85% [17,18]. The raw hydrocarbon feedstock is mostly light hydrocarbons in this case; natural gas with methane as the major component and the remaining hydrocarbons in the natural gas could be ethane, propane and butane [16].



Often, the natural gas must be treated first before the reaction and this might involve sulfur removal steps as sulfur is known to attack the catalyst in the reactor during the reforming process. Usually, this desulfurized hydrocarbon feed is mixed with superheated process steam, which must be done in accordance with the steam/carbon relationship necessary for the reforming process. The process temperatures and pressures range between 820 and 880 °C and 20–25 bar respectively, although this depends on the mode of operation. Reaction (2) and (3) are typical representation of equation (1a), which provides the highest molar ratio of H₂/CO (i.e. 3:1) and is desirable in syngas generation processes [16,19]. The primary gas produced is mainly composed of CO and H₂ with some CO₂, H₂O, CH₄ and other trace components in residual amount [16,20]. In addition, reaction (2) and (3) are different forms of steam methane reforming, which could

take place in the presence of a catalyst (nickel on alumina support or others) [8]. The reforming reactions are mostly equilibrium reactions, which means that the conversion with the aid of the nickel catalyst may approaches the maximum conversion that can be achieved at the reaction temperature and pressure [8,15]. Nonetheless, process considerations like the catalytic activity of the used catalyst, the reaction temperature and pressure, and the amount of steam applied will have major impact on the quality of the hydrogen stream produced from the process [8,15]. Furthermore, in order to increase the amount of H₂, the water gas shift reaction (WGSR) is carried out. This is to reduce the CO to form an equimolar mixture of carbon dioxide and hydrogen [16]. This step (reaction (4)) is necessary but only when preference is given to the production of more H₂.



From Fig. 4 and depending on the purpose of the reforming process, the product gas treatment and purification units may consist of several configuration of processing units like hot gas quenching unit, shift conversion unit, pressure swing adsorption unit and so on.

(b) *Steam reforming of liquid hydrocarbons.* In locations where natural gas is not available, liquid hydrocarbon for example naphtha is mostly used for the production of hydrogen [21]. Industrially, steam reforming of liquid hydrocarbons has been in use since the 1960s for the production of hydrogen for ammonia and refining processes, which is associated with the use of special catalysts, well developed desulfurization of the feedstock and improves H₂ purification processes due to many trace compounds formed as by-products [20–25]. One of the attributes of higher hydrocarbons utilization for reforming is that they are irreversibly converted into CO and H₂, and sometimes followed by the fast methanation and water gas shift reaction processes [22]. Naphtha reforming occurs at temperatures up to 850 °C [22]. [23] Has shown that fossil-derived synthetic diesel could be an option for liquid hydrocarbon. However, due to the uneconomic and complexity of the process, small scale plant operation of liquid hydrocarbon reforming has been found to be challenging for hydrogen production especially with the use of membrane reactor to have to meet the required hydrogen purity in fuel cells technology [22,26]. Another example of steam reforming of liquid hydrocarbon is the reforming of isooctane and methylcyclohexane, which were investigated over Fe- and Ni-based catalysts [27]. Furthermore, it is important to briefly discuss about steam reforming of alcohols as part of the liquid hydrocarbons. With respect to this, for efficient production of hydrogen, steam reforming of liquid hydrocarbons especially alcohol has been extensively investigated [17,28,29]. For example, small-scale hydrogen production application such as on-board fuel cell systems uses ethanol as a feed. This has been considered to be the most efficient due its possible renewable source, abundance, simple process reactions in the range of 700 °C–750 °C and the ease to transport [30,31]. In this situation, the biomass-driven alcohol provides the reduction in carbon footprint. Hydrogen can also be produced from methanol but at lower temperature (150–350 °C). This

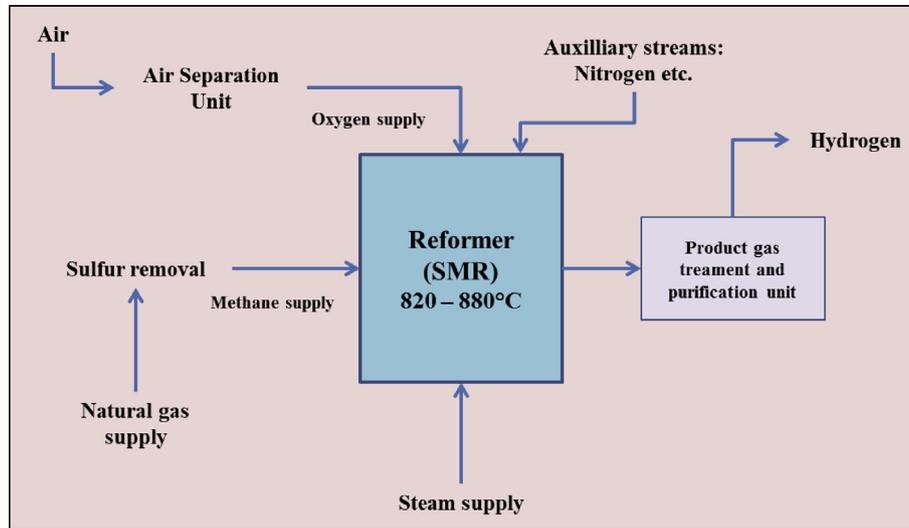


Fig. 4 – Typical process route of natural gas steam reforming.

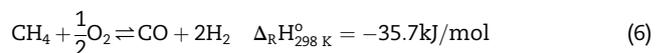
produced hydrogen in both alcohol cases are usually used for hydrotreating oxygenated derived from biomass and sometime in fuel-cell applications [4,32–34]. Amongst the alcohols, ethanol needs higher reforming temperatures to cleavage the C–C bond when compared with methanol [17]. Fig. 5 illustrates the water gas shift process (high and low temperature shifts system), hydrogen purification systems via CO abatement and pressure swing adsorption for higher quality hydrogen production in a typical ethanol reforming process [30,31].

Partial oxidation

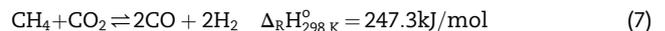
Partial oxidation (POX) of methane (natural gas) or carbonaceous compounds (hydrocarbons) is a process where the feedstock is heated in the presence of a stoichiometric amount of pure oxygen produced in an air separation unit and converted to synthesis gas according to following overall reaction (5) [16,36]:



For methane, the partial oxidation involves in-situ partial combustion of the feedstock at sufficiently high temperature, which yield syngas with H_2 : CO ratio of 2 in reaction (6) [16,37].



In partial oxidation of methane mode of operation, it is possible to have a side reaction know as dry reforming (or carbon dioxide reforming) to take place where the feed methane reacts with carbon dioxide (CO_2) to produce more syngas, thus H_2 in reaction (7) [16,38,39].



Furthermore, if there is enough oxygen in the process then, a complete oxidation of the natural gas (methane with other hydrocarbons) is possible and this can result into reaction (8) [16,40]. This usually occurs as the main reaction in the zones of stoichiometric mixture in the flame.

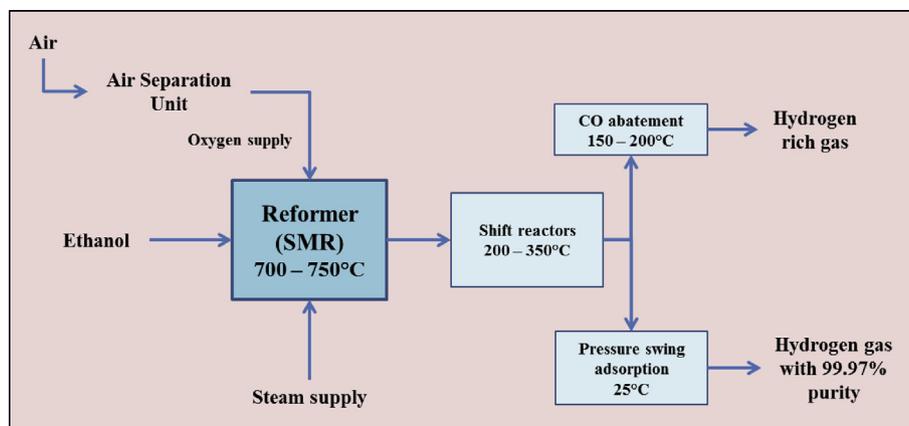
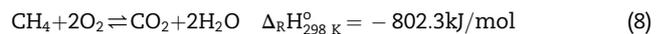


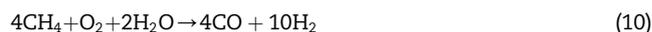
Fig. 5 – Scheme of hydrogen production via ethanol reforming route [30,35].



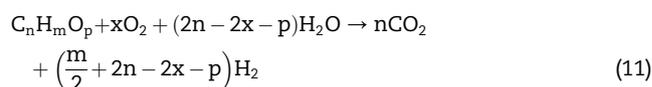
Reaction (9) presents heavy fuel oil thermal partial oxidation, which takes place under high temperature in the range of 1250 °C to 1400 °C and high pressure. Aside the use of natural gas as a major feedstock in the production of hydrogen via partial oxidation mode, the long-chain alkane present in gas oil (hexane) has also received a lot of attention over the years [1]. Other heavy feedstocks that are used in the manufacturing of hydrogen include vacuum residues and asphaltic pitch available in petroleum refineries, which are cracked to produce mainly H₂, CO and some smaller amount of CO₂, Ar, N₂, CH₄, H₂S, soot as well as ash [41]. Although, the reaction (9) is irreversible and provides lower hydrogen yield due to the fact that: the longer the chain length of the hydrocarbon feedstock; the lower the hydrogen yield. Comparing the steam methane reforming and partial oxidation of methane, the latter is known to be highly exothermic reaction and is considered faster, less efficient than the former and offer a wide range of feedstock utilization for producing hydrogen (both lighter and heavy hydrocarbons) [1,42]. To improve on the key operational process parameters and conditions relating to hydrogen in the syngas production by non-catalytic partial oxidation of natural gas, several experimental studies and numerical analysis were conducted in order to better understand the process and how parameters could be adjusted [43–47]. Fig. 6 illustrates the possible configuration of partial oxidation reformer unit for natural gas or other feedstock processing unit. Similar to Fig. 4, the product gas treatment and purification unit is also presented in Fig. 6. Technically, the illustration in Fig. 6 may be carried out as a catalytic process at about 950 °C with feedstock in the range of natural gas (methane) to naphtha or as a non-catalytic process at about 1000 °C–1400 °C with a wide variety of feedstocks like natural gas, heavy oil, refinery residue and even coal [18,48].

Autothermal reforming

Autothermal reforming (ATR) processes consist of steam reforming and partial oxidation processes. For methane or natural gas as the feedstock methane is treated with steam and in an autothermal reactor, it could be summarized to be a combination of SMR and POX according to reaction (10) and succeeded by WGS in reaction [1,2,4].



Generally, autothermal reforming of any hydrocarbon feed with the inclusion of WGS could be written in form of reaction (11) [2].



These reactions (SMR and POX) occur very fast since the exothermic reaction of the POX process can supply the required energy for the SMR reaction directly (as the reaction is autothermal). Possible temperature range in the reactor could be from 1000 °C up to 1200 °C and pressure up to 70 bars [16,40]. One of the advantages of ATR over POX is related to the H₂/CO ratio the ATR provides, which may be favorable to the downstream uses of the produced syngas. Aside this, the ATR reactor eliminates the provision of external heat supply, which could offset operating costs and investment cost on air separation unit as well as flue gas treatment and purification unit [1].

In all cases discussed in section (2.1: reforming processes), the choice of reforming process has an impact on the size of the reactor and the downstream components, units as well as the overall plant balance [31]. This selection of the reforming process must be justified with the gas treatment of the reformat and hydrogen purity requirements, heat integration as well as the potential of the optimization of operating

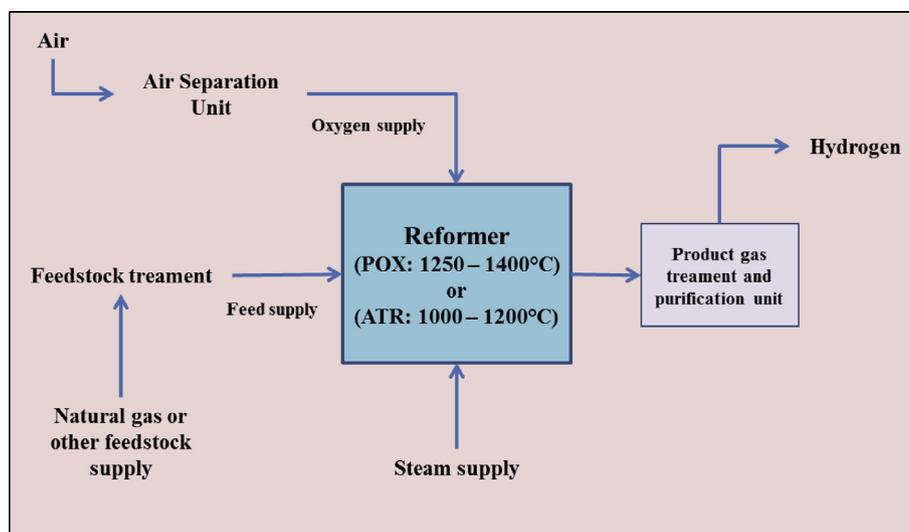


Fig. 6 – Typical configuration and process route for hydrogen production via partial oxidation or autothermal reforming of natural gas or other feedstock operation modes.

parameters [16,31]. Fig. 6 represent a schematic of an autothermal reforming of methane process assuming the reformer is on ATR mode of operations.

Table 1 summarizes possible process conditions, options from fossil based feedstock conversion and gasification processes for hydrogen generation (see Fig. 7) with possible efficiencies [3,49]. Based on industrial scale plants available in the market, the illustration in Fig. 7 is relevant for any of the carbonaceous feedstocks such as coal, petroleum refining residues, natural gas, some non-fossil based resources (like biomass and agro-wastes) and so on. Future direction in the advancement of these processes focus on high-performing reactor designs, minimal environmental impacts, process heat optimization as well as energy consumption, product gas cleaning processes and overall plant capital cost reduction.

Plasma reforming

In order to overcome the challenges like catalyst deactivation and sintering, catalyst size, weight, cost, and limitations encountered in the use of heavy hydrocarbon for hydrogen manufacturing in either SMR, POX and ATR mode; plasma reforming provides a wide variety of operating modes [6,28]. Like the conventional reforming, this technique has the possibility to eliminate CO₂ produced as the energy and free radicals used in the reforming reactions are provided by plasma generated with heat or electricity [35]. It is also one of the potential method for CH₄-CO₂ reforming as this provide lesser methane consumption aside its utilization of the CO₂ [29,50]. The plasma device can generate heat up a temperature of over 2000 °C and it make use of the enhanced reactivity of

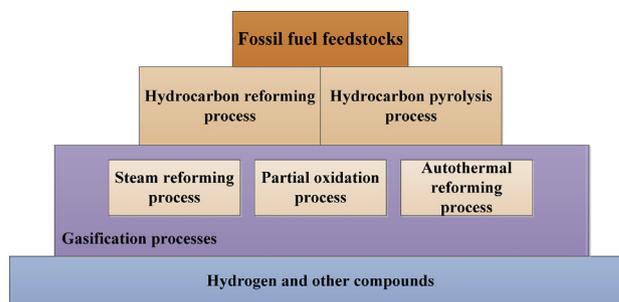


Fig. 7 – Summary of non-renewable resources conversion processes through reforming and /or gasification of feedstock for hydrogen production.

chemical species (H·, OH·, and O· radicals in addition to electrons) in the excited states present in the plasma, which is controlled by electricity [3,6]. Aside it high efficiency in hydrogen production, it is known to be an energy demanding process, which is a major factor limiting its attractiveness [3,6]. It is important to note that while the technology is being developed it has the potentials of using any of biomass waste, alcohol, methane or natural gas, diesel and others variety of fuels as feedstock [6,28,51]. With this technology, direct dissociation of hydrogen and carbon in methane or natural gas can be achieved, where the gas phase (hydrogen-rich) is collected at top and the carbon black (soot) remains at the bottom of the reactor as solid according to equation (12) [52].

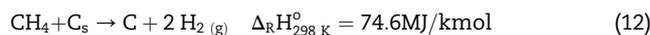


Table 1 – Comparison of major reforming processes.

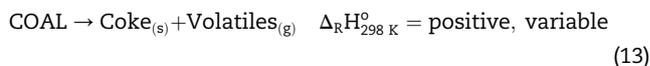
Overview and comparison of reforming processes		
Operation modes	Feedstocks (operating conditions: temperature (T) and pressure(P))	Pros and Cons
Steam reforming process	Natural gas (Endothermic conversion with steam) T = 820–880 °C and P = 20–25 bar Ethanol (700 °C–750 °C) Naphtha (at 850 °C) Efficiency = 70–85%	Pros: <ul style="list-style-type: none"> Highly advance and most applied in the industry. Highest H₂: CO ratio. It requires no oxygen. It possible to have lower temperature conditions. Cons: <ul style="list-style-type: none"> Associated with emission of greenhouse gases, trace compounds and local pollutants. Requires desulfurization of the feed
Partial oxidation process (POX)	Natural gas (Exothermic reaction with oxygen) T = 1250 °C–1400 °C Vacuum residues and asphaltic pitch T = 1100 °C–1550 °C P = 82–140 bar Efficiency = 60–75%	Pros: <ul style="list-style-type: none"> It does not require catalyst. Less desulfurization is required. It possible to have lower temperature conditions. Cons: <ul style="list-style-type: none"> Very high temperature process. Low H₂: CO ratio. Formation of soot and it handling makes the process complex
Autothematl reforming (ATR)	Natural gas (Autothermal process with steam and oxygen) T = 1000 °C– 1200 °C P = 70 bar Efficiency = 60–75%	Pros: <ul style="list-style-type: none"> Low operating temperature than POX Combine SMR and POX processes Heat from POX is used for SMR Cons: <ul style="list-style-type: none"> It needs oxygen or air

Gasification of coal for hydrogen

For efficient beneficiations of carbonaceous hydrogen-containing feedstock, gasification is a thermochemical transformations and one of the key technologies in commercial production of synthetic gas from solid feedstocks like coal, petroleum coke, biomass (a renewable resource) and other carbon containing compounds [6,53]. There are different varieties of gasification processes available in the industry. Based on the contact between the gas and feedstock (e.g. coal), gasifiers are categorized into: fixed or moving bed gasifier (counter of current), entrained bed gasifier, fluidized bed gasifier, plasma gasifier and so on [54].

Coal-based hydrogen production has been applied over several decades before other fossil-based resources. When the cost of natural gas is high, hydrogen produced from coal can be economical and competitive without much consideration on the type of gasifier applied. Coal gasification process converts the solid coal into gaseous phase know as synthetic gas, which is an important step in clean coal technology. Depending on the process, the coal is partially oxidized with any of the gasifying agent: air or a mixture of oxygen and water vapor or carbon dioxide, which is used as the oxidant at elevated temperature in high-pressure reactor to produce mainly hot gas containing H₂, CO, mixture of many gases with steam, CO₂, ashes and other materials [1,52]. The performance of the gasifier depends on the operating pressure [1]. The produced gases can be burnt to produce energy (after cleaning) in form of syngas-to-electricity for combined power cycle integration or mostly chemically converted to products (after cleaning) like fuels and chemicals via syngas-to-hydrogen, fuels or chemicals, if combine with membrane separator and water-gas shift reactors [53,55]. Usually, these combination of processes are typical to the integrated gasification combined cycle (IGCC), where high pressure gasifier converts coal and other carbon based feedstocks into pressurized synthesis gas. In the downstream sections of these gasification plants, hydrogen concentration needs to be increased by removing impurity gases or application of gas cleaning methods in order to increase hydrogen purity for further

downstream applications. When coal is supplied into gasifier and depending on the type of coal, the coal pyrolyzes to coke and volatiles at 700 °C–800 °C in the gasifier according to reaction (13).



During coal pyrolysis, the content of the products depend upon the temperature, pressure and gas composition and it is expected to produced light gases such as CO, CO₂, H₂, steam, CH₄, tar and char as represented in equation (14) [54]. The char is made of mainly solid residue (carbon) while the tar is composed of heavy organic and inorganic compound that exist as viscous liquid and are known to be corrosive [54].



Furthermore, several chemical reactions that occur in the gasifier system can be summarized into heterogeneous and homogenous reactions in Table 2 [49,53,56]. Beside these reactions, there are other forms that take place in the gasifier such as those of sulfur present in the coal reacting with steam (H₂O) and methane leading to the formation of hydrogen sulfide.

Presented in Table 2 are the dominant heterogeneous and homogenous reactions that take place in the gasifier system. The scheme in Fig. 8 represents the considerations required for coal or other feedstock (like biomass) gasification for hydrogen production. The feedstock preparation differ among the various possible feeds (size, drying etc.) to be supplied into the gasifier, the gasifiers also differs so as the operating parameter like temperature, pressure, feed flow rate, gasifying agent and the gasifier downstream units required for ash handling, product gas treatment as well as gas cleaning. With development of several initiatives and technologies on carbon capture, utilization and storage (CCUS), the inevitable higher carbon content of coal results into higher CO₂ production and its emissions continues to be major concerns when compared to other hydrogen production from other fossil and non-fossil based resources as well as their respective production technologies [52].

Table 2 – Some heterogeneous and homogenous reactions that are expected during coal gasification.

Reaction type	Reaction	Standard enthalpy of reactions ($\Delta_R H_{298\text{ K}}^{\circ}$)	Equation number
Heterogeneous reactions			
Endothermic reversed Boudouard equilibrium process	$\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$	172.6 kJ/mol	(15)
Exothermic hydrogenation leading to methane formation	$\text{C} + 2\text{H}_2 \rightleftharpoons 2\text{CH}_4$	-74.9 kJ/mol	(16)
Exothermic oxidation leading to CO formation	$2\text{C} + \text{O}_2 \rightleftharpoons 2\text{CO}$	-221 kJ/mol	(17)
Exothermic combustion leading to CO formation	$2\text{C} + \text{O}_2 \rightleftharpoons 2\text{CO}$	-393.6 kJ/mol	(18)
Endothermic heterogeneous water-gas shift reaction	$\text{C} + \text{H}_2\text{O} \rightleftharpoons 2\text{CO} + \text{H}_2$	-131.46 kJ/mol	(19)
Homogenous reactions			
Exothermic oxidation of CO ₂	$2\text{C} + \text{O}_2 \rightleftharpoons \text{CO}_2$	-565.5 kJ/mol	(20)
Exothermic water-gas shift reaction	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	-41.2 kJ/mol	Similar to (4)
Exothermic conversion of CO to methane (methanation)	$\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$	-206 kJ/mol	(21)
Exothermic combustion of methane	$\text{CH}_4 + 2\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O}$	-802.3 kJ/mol	Similar to (8)
Endothermic methane decomposition	$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$	206.2 kJ/mol	Similar to (2)

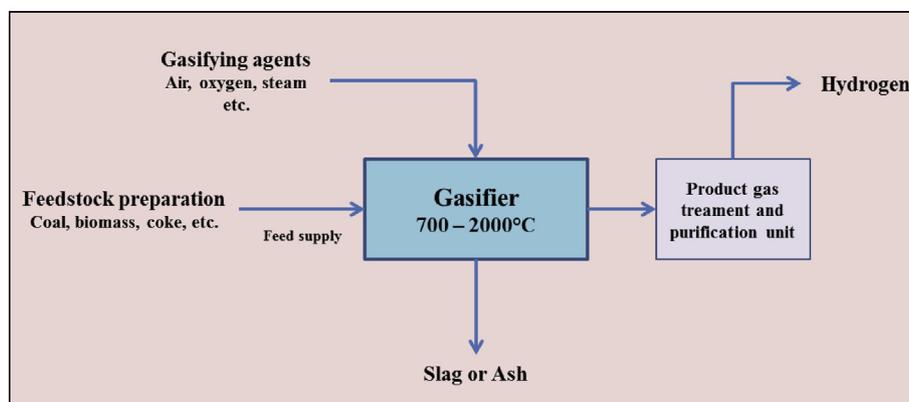


Fig. 8 – Illustration of coal gasification for the production of hydrogen.

Emerging developments in industrial scale reforming units

(a) Combination of reforming unit with electrolysis plants

Some of the advancements in steam reforming process technologies are now receiving a lot of attentions. Renewable electricity from solar and wind could be integrated with reforming unit (also possible for gasifying units for oxygen supply) whereby replacing the conventional electricity production from fossil resources. This could be possible at places where electricity price is low and natural gas price is high. In this case, electrolysis process utilizes the excess and cheap electricity from renewable solutions, which is integrated in combination with steam reforming unit (see Fig. 9). Since some reformers are oxygen blown reformers, then the oxygen from the water splitting can be used by the steam reforming unit. The benefit of this is that, the electrolysis unit uses cheap and excess electricity from solar and/or wind, produces on-site hydrogen on a large scale and sells oxygen, which is a usual common waste with less values.

Usually, the oxygen required for the reforming (or gasifying) units are purchased in several volumes of cylinders and transported by truck to the plant site, which at the end of the operations result in the increase of operating and hydrogen production cost. This could bridge the economic attractiveness of large scale high temperature electrolysis unit and reforming unit. Also, in most gasification units, oxygen may serve as the gasifying agent, which could be sourced from the electrolysis process and thus, avoid the cost of air blowers (see Fig. 9).

The overall efficiency of the combination of electrolysis unit and reforming unit is significantly increased by reducing utility cost on water and its consumption; lessen concerns and the level of CO₂ emission into environment and at the same time producing mass production of hydrogen for on-site use or for sale. In this type of scenario (according to Fig. 9), it is possible to have the steam supply from the concentrated solar power (CSP) system as well as the electricity supply it offers. Similar trend can be found with many process design, engineering and service companies' proprietary technologies. Haldor Topsoe is one of the examples in this technological development (see Fig. 10). Fig. 10 illustrate the cost benefit potential of steam reforming unit integrated with electricity

from solar or wind, which then supplies the electrolysis unit compared with the conventional (traditional steam reforming unit) as illustrated in Fig. 9. Fig. 10 shows the optimal curves (blue lines) and the hydrogen price (in \$/1000 Nm³) reduction potential for SMR with electricity integration – optimal and traditional steam reforming – optimum when natural gas price was assumed to be 3.5 \$/mmBTU as against electricity cost (in \$/kWh).

(b) Heat integration and waste heat recovery

In the overall reforming unit plant layout, optimization strategies have provided many plant operators to improve efficiency in their plant heat exchanger network. New designs of reformers like heat exchange reformer based on considerations like efficient heat transfer, pressure drop, temperature profile, material selection etc. are based on internal heat exchanger reformer tube arrangement. In this development, the hot reformed gas flows through the inner tube arrangement and counter-current to the feed supply over the catalyst bed in order to provide the heat required for the reaction. Air Liquide, Haldor Topsoe and other companies have demonstrated this in their commercial products. High pressure steam produced in this typical reforming unit is used within the reforming unit and the surplus is sold to other users. In another case, for efficient production of hydrogen in new steam reforming units, there are many options that could be adopted in order to reduce the amount of steam produce, which may be in excess for export or for sale. Generally, energy integration and optimization of heat exchanger networks could reduce the steam demand of reformer plant. The application of pre-reformer with reheat (waste heat recovery unit) could be used to preheat the reforming unit feed and to produce the required steam and providing such entire reforming plant with reduced steam production in its boiler unit(s). Ultimately, all these optimization strategies, if strategically and technically harnessed could result in low operating expenditure (OPEX) and low capital expenditure (CAPEX).

(c) Facility size and cost reduction

Modularized plants and small-scale reforming units for on-site hydrogen production continue to attract new producers. These sets of production facilities exhibit features like

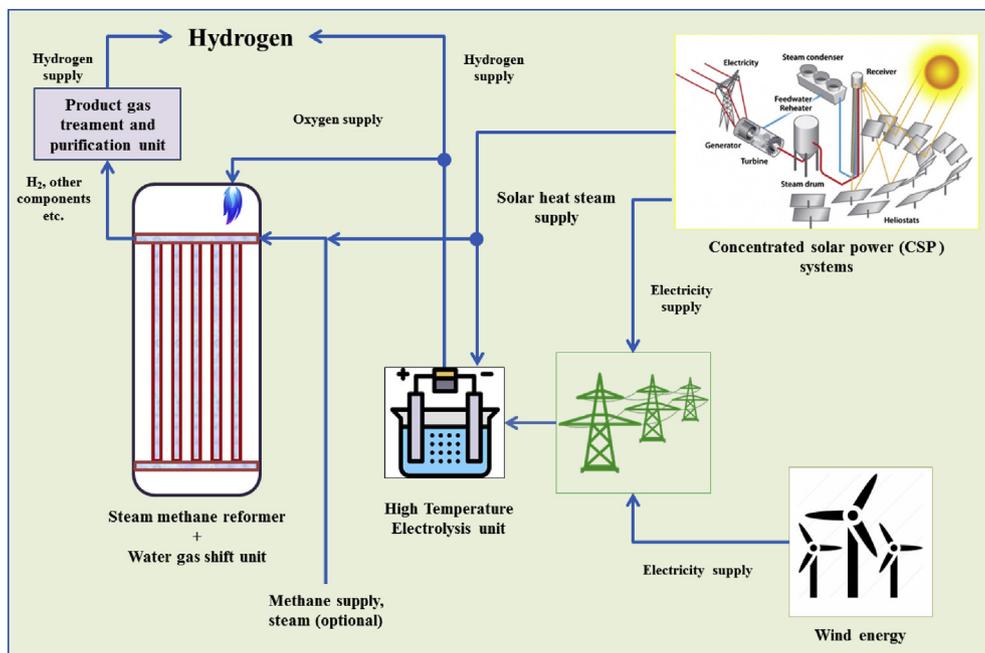


Fig. 9 – Possible options in integrating high temperature electrolysis unit with steam methane reformer while electricity is supplied by solar or wind energy.

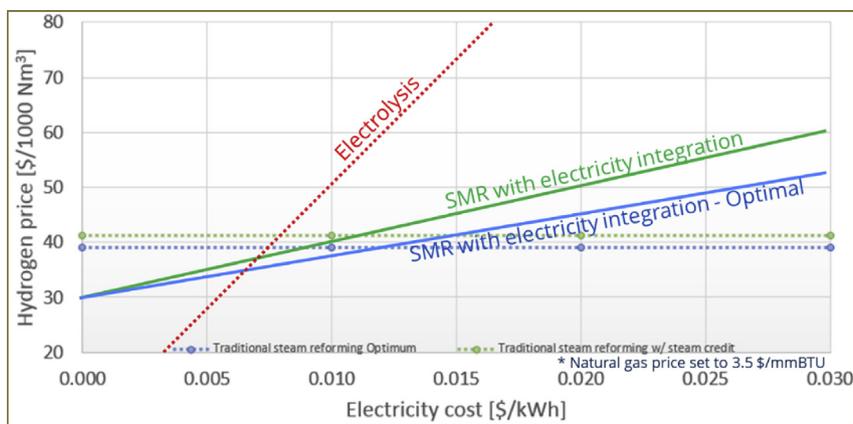


Fig. 10 – Cost potential of electrolysis in combination with steam reforming - Hybrid solutions by Haldor Topsoe [57].

improved plant performance and reduction of hydrogen production costs for large volumes for on-site reformer units, which could be applied at remote locations. In these categories, efficient and slim reactor design with well improved burner technologies are now replacing the larger scale plant especially in the gas-to-liquids (GTL) technologies to produce syngas from reforming natural gas, liquefied petroleum gas (LPG), naphtha and refinery gas. In addition, these small scale plants are integrated with renewable energy solution for the production of hydrogen and other chemicals like methanol, ammonia and fuels.

Techno-economic studies of this small scale plants based on capital cost of equipment have proven their viability. The original costs of an existing plant and its capacity can be

estimated considering the cost increase by time based on the Chemical Plant Cost Index in equation (22).

$$C_{\text{Invest, year}} = C_{\text{Invest, ref}} \left(\frac{X_{\text{cal}}}{X_{\text{ref}}} \right)^m \left(\frac{I_{\text{CEPCI, year}}}{I_{\text{CEPCI, ref}}} \right) \quad (22)$$

Where:

$C_{\text{Invest, year}}$ = cost of plant or section for new capacity = Capital cost

$C_{\text{Invest, ref}}$ = cost of plant or section of reference or original capacity

X_{cal} = capacity of plant or section of new requirements

X_{ref} = capacity of plant or section of reference or original requirements

$I_{CECPI, year}$ = index value for the particular year

$I_{CECPI, ref}$ = index value for reference year of original capacity.

m = cost exponent (or capacity factor)

Analysis of development gaps in high temperature hydrogen production pathways

Fig. 11 illustrates an overview of several high temperature hydrogen production technological pathways from renewable and fossil based resources and their status in the industrial scale deployment to the market for commercial operation as well as their hydrogen production capacity (by volume). The blue boundary line demarcates the commercialization gaps required and industrial scale readiness for each technology as well as their high temperature range or process heat requirements.

On the right hand side are the most advanced namely steam reforming process and coal gasification for hydrogen production.

Technologies for reforming of natural gas and other hydrocarbons are widely used in the industry. Current research and development focus on small-scale modular technologies in order to support the development of small scale reformer and reactor designs that offer efficient, economical, decentralize production of syngas and hydrogen to be delivered to the market. The high hydrogen-to-carbon ratio of natural gas (methane) continues to make it the best candidates amongst the other fossil feedstocks aside the inexpensive supply of natural gas as well as the established distribution infrastructure. The modular scale reactor for steam methane reforming provides the opportunity to have equipment cost reduction, which at the long run may result into the low cost of hydrogen production.

Improved catalyst to provide high yield as well as improved feedstock pre-treatment to have efficient conversion are been explored for significant operating, maintenance and capital cost reduction in order to increase process equipment system reliability.

Furthermore, the lower efficiency and high capital cost continues to make gasification of coal for hydrogen production not as attractive as that of steam methane reforming. Coal gasification requires ash and other solid residues removal during operation, which has limits its application for modular system and as such it must be a large-scale centralized plant for hydrogen production. Although, the continuous improvement in the integrated gasification combined cycle (IGCC) has provided the opportunities to remove impurities from the syngas prior to the power generation cycle, which give the benefit for sulfur to be reused via the Claus process and lower other emissions of sulfur dioxide, particulates, mercury, and possibly carbon dioxide if there are plans for Carbon Capture, Utilization, and Storage (CCUS) technologies. In all these advancements in coal to hydrogen production, the overall plant availability continues to result into higher capital and operating cost.

On the left hand side are technologies that are still at research and development stages, although there are wide interests across the globe based on the potentials these technologies offers in the production of hydrogen.

The developments of plasma reforming continue to provide the opportunity to utilize both fossil base resources like methane pyrolysis and renewable resources like ethanol using plasma or plasma-catalytic technologies for hydrogen production. Though, these plasma-based processes are more expensive than steam reforming processes but they have the benefit of utilizing CO_2 and carbon as feedstock for the production of carbon black, carbon fibers, which could be sold to improve plant profitability.

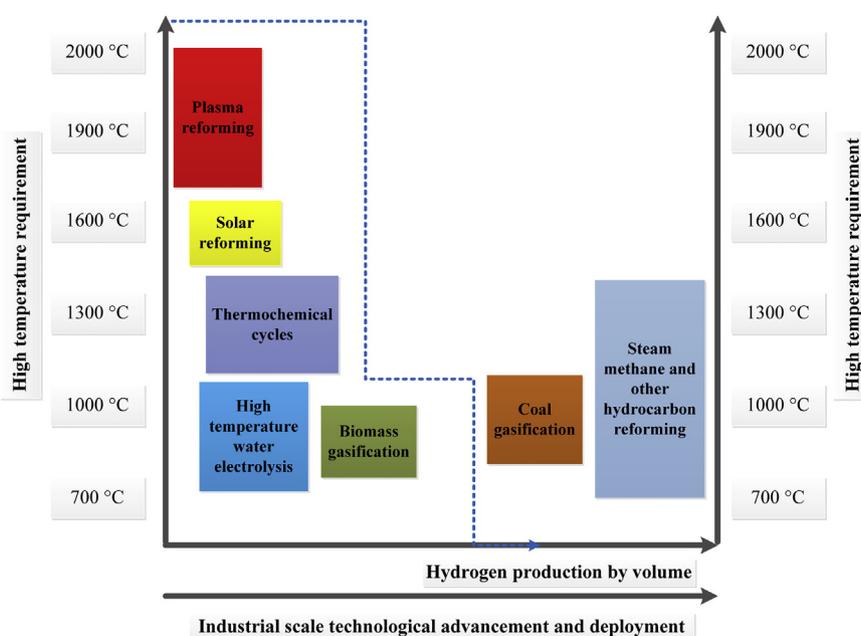


Fig. 11 – Major high temperature hydrogen production technological pathways, production by volume and their industrial status.

Nonetheless, continuous research and development in the area solar reforming technology over the years are gradually showing market potential for the use of solar thermal energy from concentrated solar power (CSP) to drive chemical reforming reactions by which hydrocarbons especially natural gas are converted to syngas. With the gradual emergence of the solar reforming technology, which could provide lower cost of hydrogen in the market and more CO₂ emission reduction is possible when compared to the established technology like steam methane reforming and coal gasification. This technology offers an intersection in the utilization of fossil based resources (e.g. natural gas) by renewable energy technology (solar) to produce hydrogen only if the natural gas is not synthetically manufactured (more detail in sub-section [Other prospective technologies for hydrogen production](#)).

Currently, there are no commercial thermochemical cycle process plant for decomposition of water into H₂ and O₂ in the market. Numerous cycles that have been proposed and under investigation are at experimental and development phases, the process still have the potential of producing hydrogen at high temperature. With heat source from nuclear and solar, thermochemical cycles could become significant in the renewable energy mix and in the production of hydrogen in the next decades.

High temperature water electrolysis is another promising technology to produce hydrogen with electrochemical reactions to split water into H₂ and O₂ when the primary energy source is solar. This technology can be applied to electrolyze different compounds like CO₂ and water to produce syngas in order to complement excess renewable energies through power-to-gas or/and power-to-chemicals process routes.

The wide availability of biomass resources from agro-produce or agro-waste, organic residues from animal waste, municipal solid waste and the likes; after biogas have been produced have made biomass an important resources in the renewable energy mix and hydrogen economy. Well-developed gasifier units for biomass gasification are nearly identical to those of coal gasifiers aside their different feed preparation methods. These biomass-derived resource gasifiers operate at over 700 °C and depend on expensive materials for plant construction. Biomass resources offer a wide range of techniques for the production of hydrogen and have great potential for industrial scale application. Also, biomass can be used to produce bio-derived liquids as well as biogas, which in both cases could be used in reforming processes in order to produce hydrogen. Industrial fermentation and microbial electrolysis are some of the biological-based technological pathways biomass offers in hydrogen production. More overviews of development trends and technological status of all the discussed high temperature hydrogen production are shown in [Fig. 11](#).

Other prospective technologies for hydrogen production

In addition to the development gaps in high temperature of hydrogen production, this sub-section shall look into soon-to-be technologies, which interplays between the potentials and applicability of renewable and non-renewable energy resource. There are several technological developments in these areas across the globe.

(a) Solar-aided natural gas or bio-methane reforming

Natural gas is reformed in an identical conventional process like industrial steam reforming. Here the heat source is from solar irradiation providing the high temperature reaction heat for the methane decomposition to produce hydrogen and carbon monoxide. Although, the natural gas is from fossil-based resources, this technology has the potential of reducing CO₂ footprints and lowering cost of production as to the case of conventional steam reforming process. The EU-Project SOLREF, which is a 400 kW scale has demonstrated the potentials and efficiency benefits for hydrogen production. When bio-methane is reformed, the carbon footprint is expected to be lowered than that of the natural gas reforming.

(b) Solar-aided dry reforming

Similar to the solar natural gas reforming, here the dry reforming reaction already discussed in reaction (7) takes place with carbon dioxide as one of the main feed in the reforming process. Aside the production of hydrogen and syngas, here the greenhouse gases are utilized and consumed. With this technology, solar-hydrogen, chemical and fuels are assured especially when integrated with large CO₂ emitting industrial process like cement production. This technology also offers less use of natural gas as compared to the conventional steam reforming processes.

Future outlook for hydrogen production

Some of the factors that are expected to drive hydrogen market growth vis-a-vis the increasing hydrogen usage and demand are:

- its use as raw materials for the production of chemicals (methanol, ammonia, etc.) and carbon-neutral or carbon-free transport fuels,
- the possibilities of producing hydrogen from a wide range of raw materials available everywhere especially water, biomass etc.,
- increase in the acceptance of fuel cell electric vehicle (FCEV) by many countries,
- increase demand for hydrogen in petroleum refining processes,
- increase in the decarbonisation of transport, industry like steel producing plants and gas grids,
- adoption of hydrogen-to-power based on fuel cells,
- increase demand in iron and steel requires hydrogen for annealing process and others.

Being a mature technology and proven method developed several decades ago, steam reforming is expected to continue to dominate the highest production share. Every large refinery operation depends on steam reforming, which accounts for the largest production source across the industry. Clean coal technologies are been improved upon for hydrogen production based on different gasification methods available. High temperature water electrolysis through renewable energy accounts for the most environmental friendly source of hydrogen followed by biomass gasification. In the hope of

providing sustainable energy, renewable resources and renewable feedstocks shall play a key role in the hydrogen economy. Further research and development in various solar-to-hydrogen processes through water splitting processes and thermochemical cycles shall be important game changer in the renewable energy mix.

Conclusion

Hydrogen production technologies are being promoted and further developed as it is evident that there is a growing demand across the globe on various applications. In these assessments, different hydrogen production pathways from non-renewable resources were discussed. Advanced steam reforming technologies will continue to be the dominant technology in hydrogen production. Potential technological development and researches have provided several pathways for the production of hydrogen at industrial scale when integrated with renewable solution like electrolysis. The largest demands for hydrogen are from petroleum refining, petrochemical industries, fertilizer production, the steel industries and recently the mobility industry; whereas all continues to contribute to the further growth of hydrogen production and utilization worldwide. Emerging solar-aided reforming processes with the application of Concentrated Solar Power (CSP) have shown remarkable benefits. Besides the all these technological assessment (less energy usage, emissions and environmental impact) of any of these hydrogen production processes, the favorable cost (per kg of hydrogen) and techno-economic benefit of any of these technologies shall impact on the hydrogen infrastructure and production value chains.

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