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The future of hydrogen: Challenges on production, storage and applications

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ABSTRACT

With the demand for hydrogen being expected to increase by about 8-folds in 2050 over 2020, there are several factors that can turn into challenges for effective roll out of hydrogen applications in energy sector. Hydrogen has the second highest calorific value, 120-142 MJ/kg, which is the best energy-weight ratio among all conventional fuels. Among all hydrogen production processes, the green hydrogen production through mature water electrolysis process, with technology readiness level of ~7-8 (demonstration/system development) and commercial readiness index of ~ 4-5 (deployment) contributed about 30% to market share with efficiency of 55-80% and production cost of ~ \$4-7/kg H_2. This study found that the current hydrogen production costs may reduce to desired 1-2 \$/kg H_2 within a couple of decades, but there is still a lack of plans for combining various hydrogen production processes where necessary, rather than only focusing on producing hydrogen in mass scale. Among all the hydrogen storage systems, the specific volumetric storage cost of metal hydride is less, about \$125/m^3, than other systems. Ammonia has lowest specific energy cost, about \$13/GJ amongst other storage systems. There is a requirement of rapid progression in relevant infrastructure development for efficient supply chain management for storage, transportation, and delivery of hydrogen to the stakeholders. This paper reviewed 400+ articles and summarised hydrogen production processes, storage options, production costs and applications. The synthesis of key information and deep analysis of limitations of existing studies has been provided followed by deep discussion on the challenges of hydrogen as energy carrier for future. To achieve sustainable development goals, integrated plans, infrastructure development, reduction of production costs, achieving net zero emissions and novel storage development need to be achieved within 2050. This reviews thus could be used as a guideline by policymakers, researchers, and scientists for shaping future of hydrogen.

1. Introduction

Hydrogen is now considered to be the future form of leading energy system and multipurpose industrial raw material due to its significant potential to shape building a cleaner and sustainable earth for the human being. There are various production pathways (i.e., electrical, thermal, hybrid, and biological) for hydrogen generation from various feedstocks [1,2]. That is why, optimal integration of all of these pathways based on regional variation of feedstocks and technical resources can efficiently make hydrogen a potential energy transformer and lower the emissions significantly to achieve the sustainable development goals (SDG) [3-5]. Apart from the conventional fossil feedstocks biodegradable and non-biodegradable wastes can be used to produce hydrogen by improving the waste-to-energy producing pathways [6-9]. Using wastes can be considered as net-zero emission producing feedstocks. Integrating carbon capture, utilisation and storage (CCUS) in the hydrogen production system from the wastes can solve multiple problems, i.e., sustainable waste management, emission reduction, and cleaner fuel production. With about 13.5% recycling rate of wastes around the globe there may be about 3.4 billion tonnes of solid waste generation by 2050 which is about 70% more than that of year 2016 [10]. Also, the overall quantity of solid wastes generated by 2050 may lead to emission of more than 2.6 giga tonnes of CO_2-e [10]. The techno-economic progress of coal gasification process [11,12] can help to accelerate the establishment of large-scale commercial gasification of wastes [13] for decarbonised hydrogen production. Begum et al [14] developed a numerical model and investigated the pyrolysis of municipal solid waste. Also, the pyrolysis of wastes for energy production can be integrated with the reforming process to produce hydrogen [15,16]. Efficient use of catalysts [17,18] along with optimisation of operating parameters [19] are also undergoing extensive research works to

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Nomenclature

AHW	Atomic hydrogen welding
APR	Aqueous phase reforming
ATR	Autothermal steam reforming
BTH	Biomass-to-hydrogen
BWGS	Bio-water-gas shift
CAPEX	Capital expenditure
CCU	Carbon capture and utilization
CCS	Carbon capture and sequestration
CODH	Carbon monoxide dehydrogenase
COS	Carbonyl sulphide
CRI	Commercial readiness index
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CSP	Concentrated Solar Power
CSR	Catalytic steam reforming
CTH	Coal-to-hydrogen
DRM	Dry reforming methane
EBS	Environmentally “benign” sequestration
EOR	Enhanced oil recovery
EWGS	Electrochemical water–gas shift
FCEV	Fuel cell electric vehicle
FCV	Fuel cell vehicle
GHG	Greenhouse gas
HFCV	Hydrogen fuel cell vehicle
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
LTS	Low temperature shift
LOHC	Liquid organic hydrogen carrier
LH_2	Liquid hydrogen
MCFC	Molten carbonate fuel cell
MeAFC	Metal-air fuel cell
NERA	National Energy Resources Australia
OSR	Oxidative Steam Reforming
OPEX	Operating expenditure
PEFC	Polymer electrolyte fuel cell
PEM	Polymer Electrolyte Membrane
POX	Partial Oxidation
PSA	Pressure swing adsorption
P2G or PtG	Power-to-Gas
PEMFC	Proton exchange membrane fuel cell
PAFC	Phosphoric acid fuel cell
SCWR	Supercritical water reforming
SI HEV	Spark ignition hybrid electrical vehicle
SI ICEV	Spark ignition internal combustion engine vehicle
SO	Solid Oxide
SR	Steam reforming
SOFC	Solid oxide fuel cell
TRL	Technology readiness level
UNIDO	United Nations Industrial Development Organization
USDOE	United States Department of Energy
WGS	Water-gas shift
WFPP	Waterloo flash pyrolysis process

produce high percentage of hydrogen from thermochemical and biological processes [20]. Rapid growth in technologies have been observed in recent years along with advanced economic analyses to produce hydrogen commercially at an affordable level of total cost of ownership (TCO) [4,5,21].

The extensive deployment of hydrogen production facilities via currently available mature electrolysis processes can be coupled with various energy utilising sectors and efficiently achieve decarbonisation [22,23]. In addition, countries which produce extra renewable energy can use that to produce hydrogen and export or transport it to other regions of the world as green energy in the form of compressed hydrogen gas or liquefied hydrogen or in other carriers like ammonia or methane [22]. This process is currently referred to as “Power-to-Gas (P2G or PtG)” technology [24,25]. There are two key challenges to make the vision successful: firstly, establishing a market for hydrogen and secondly, decarbonising the hydrogen production processes to restrict the emissions from across sectors [22]. There are several factors for hydrogen production rather than any mutual exclusiveness between these two key challenges for hydrogen deployment for cleaner climate condition and energy supply. These factors are production capacity improvement and market size development, support from governments and investors, feedstock selection, and economically feasible technology selection for production, decarbonisation, storage, transmission and applications, which are influenced by the hydrogen industry establishment. In reality, without economically beneficial and efficient decarbonisation processes, the hydrogen production processes from various feedstocks other than wind, solar and nuclear energies will not be considered as clean fuel [26-29].

In spite of several unsuccessful efforts at campaigning for hydrogen to be considered as a clean energy producing fuel in the various sectors previously, there are positive expectations about the successful implementation of hydrogen infrastructure due to demonstrated successes of alternatives like fossil fuel conversion to compressed natural gas, renewables like solar photovoltaic (solar PV), wind, energy storage systems, hybrid and electric transportation systems [30-33]. In order to integrate the hydrogen in the energy-economy system, total hydrogen supply chain needs an effective set of optimal and low-cost technological evolution for massive scaling-up of hydrogen production, storage, transmission and distribution purposes [34-38].

The physical and chemical properties of hydrogen have made this beneficial energy vector highly challenging to store and transfer economically for mass application in comparison to other existing energy sources in recent times. The lower volumetric and energy densities of hydrogen at room temperature, compressed (700 bar) and liquid conditions are 0.0107 MJ/L, 5.6 MJ/L, and 10.1 MJ/L respectively considering higher heating value of 143 MJ/kg [39] have made the storage system highly challenging. Besides, the highly active electron of hydrogen has made it highly susceptible to the metal storage systems which is known as “hydrogen embrittlement” [39,40]. Hydrogen can be stored physically through phase changing or through surface adsorption or absorption processes [39,41]. Ziver et al. [42] have recently reviewed underground storage options of hydrogen gas and indicated that the salt caverns, and saline aquifers offer better technical efficacy than the depleted oil reservoirs to prevent loss of hydrogen due to chemical reactiveness with residual oil. Besides, the depth, types of rocks, and permeability are other issues to decide scale of hydrogen storage into underground facilities. Based on the applications of the hydrogen in the energy transformation systems (i.e., scaling-up [34], mobile, or stationary [35,36]), technology implementation and various infrastructures planning in regions worldwide [43-46], there are opportunity to utilise cost-efficient hydrogen storage processes [47] as a form of energy storage in renewable way. Though currently almost all hydrogen production from the fossil fuels do not use CCUS processes (i.e., grey hydrogen), there is a high demand of efficient and large scale CCUS facilities (about 50 giga tonnes by 2050 [5]) to be integrated with the emission producing processes to produce blue and green hydrogen for decarbonised energy scenario and reduce overall levelised cost of hydrogen production and deliveries (LCOH).

IRENA [48] has recently summarised the factors those have been impeding the scaling up of the hydrogen production in recent years to achieve greener transformation of energy sector. These are the costs of establishment and ownership, technical matureness, and lower efficiency in each of the value adding stages, insufficient progress for renewable electricity generation, uncertain policies and regulations, lack of common institutional standardisation and certification processes, and chicken-and-egg crisis in establishing the reliable infrastructure for hydrogen production and supply chain management. Indeed, the key concern of transforming the hydrogen as fuel for energy production to replace the emission intensive energy sources for the energy consuming sectors has been found to be the costs due dependence of all other factors on it [48-51]. Time is another key factor as there is potential of complete transformation of costs as well as other factors from medium-term projection (until 2030) to long-term projection (2050 and beyond) [52].

In order to develop the novelty of this review article the Clarivate Web of Science database has been used to find out the current reviews on hydrogen by using few key words (e.g., title including - “Hydrogen”, document type - “review”, web of science category - “Energy Fuels” or, “Electrochemistry” or, “Engineering Chemical”, publication years – “2020, 2021, 2022”), which yielded 569 review articles. Though are numerous review articles on various production technologies, there are only a few articles which have reviewed the production, storage, transportations technologies altogether along with the critical goals, policies and projection which are indeed driving the key development requirements of hydrogen supply chain [53-56]. Table 1 presents reviewed information on combined sectoral effect for hydrogen supply chain. However, Faye et al. [38] reviewed various production technologies, storage, and transport options to identify the overall cost/kg and found that hydrogen can be supplied at a cost of \$2.86/kg when tube trailer are used for transportation after hydrogen production through efficient production process and implementing CCUS. With ever increasing risk of financial crisis all around the world, increasing living cost people may not be ready to pay higher cost for cleaner fuel unless there is clear indication of lowering cost of renewable energy through technology development transition period. Lebrouhi et al. [57] stated in their review that about 60% of the global GHG emissions reduction will be driven by the renewables in the later phase of the transition period. But this will only occur when there is efficient coordination and decision making through respective parties within the energy transition chain. Hence, it not only the technology but also the maturity of policies and planning which should happen within a very short period to allow reliable progress of the technology development processes. During these periods, the fossil fuel fed thermochemical processes should be economic enough to compete well in the energy mix. Gonzalez-Garay et al. [58] reviewed on overall hydrogen supply chain for mobility and forecasted that the currently valued at \$6.0/kgH_2 from renewables will drop to about \$2.6/kgH_2 by 2030 if there are optimal prospect in the challenging areas like electrolyser’s efficiency, higher investment with lower interest rate, and rapid technical maturity. With future goals, it is highly essential to go through overall technical review on production, storage, and applications to propel the growth all around. The more the explorations there is a chance of obtaining effective solution within anticipated timeline. Investment, public awareness and infrastructure maturity can control how the hydrogen will enter into domestic and international market for a prospective producer of renewable hydrogen, for which Australia may enter into international market before it enter into the domestic market with renewable hydrogen [59].

Though hydrogen production, storage, and applications have been reviewed earlier, the rapidly evolving projections and energy marketisation due to technological progress, economic analyses, and relevant policies have attracted necessity of reviewing again. Thus, this paper analysed and reported different aspects of hydrogen usage such as production processes, storage, distribution, applications, sustainability, and cleanliness based on the energy sources and feedstocks that may help progressing towards future goals. Besides, global scenarios of hydrogen and the related research and development are discussed here. Finally, the challenges of utilising hydrogen and the technology

Table 1
Recent review articles on hydrogen production, storage, and applications

Reference Article	Reviewed Areas	Why this review?	Key Information
Chau et al. [53]	Hydrogen Production through reforming (steam methane, autothermal, partial oxidation), electrolysis (alkaline, polymer electrode membrane, solid oxide electrolyser)	In order to determine the comparative efficacies of the reviewed technologies from the available data by using modified multi-criteria decision-making (MCDM) analysis.	Maturity of technology and decision-making through parametric analysis like design improvement, operating conditions, yields, infrastructure capabilities, and resource management analysis.
Faye et al. [38]	Hydrogen production, storage, and transportation processes.	To identify the most prospective and effective process technologies which will bring good impact to future hydrogen goals.	Partial oxidation reforming process is efficient along with CCUS technology when fossil fuels are used as feedstock. Carbon deposition can be removed from catalysts with CeO_2/ZrO_2 support. Tube trailer transporting can be more efficient than the liquefied hydrogen.If Hydrogen is to be blended with natural gas, it is effective with concentrated hydrogen.
Dawood et al. [60]	Renewable hydrogen – production, storage options, safety concerns, and uses.	Due to absence of a single review article which reviewed interlinks among these areas.	It is necessary to link these reviewed areas along with the purification process, which indeed defines the cleanliness level of the hydrogen.
Yue et al. [54]	Electrolysis, fuel cell power conversion, storage of energy in the form of hydrogen, transportation.	To integrate the energy system with the hydrogen production system, energy-hydrogen-energy conversion for application requirement and transport.	The power to hydrogen, and hydrogen to power mainly linked to cost, efficiency, investment, production scaling up, and policy support.
Sazali et al. [61]	Hydrogen production and applications.	To investigate the existing technological capabilities and necessary improvements as defined by economic development.	More demand of hydrogen production will influence the currently high-cost energy values to be dropped down, which will also influence the cost reduction of renewable hydrogen production along with storage facilities .
Kannah et al. [55]	Hydrogen production, cost-effectiveness of the technologies.	To investigate the global energy market share potential of hydrogen by mixing various production and purification processes along with	Rate of return, capital cost, and feedstock cost will influence the hydrogen cost. Since the renewable is still expensive the highly efficient reforming

(continued on next page)

Table 1 (*continued*)

Reference Article	Reviewed Areas	Why this review?	Key Information
		cost of production through detailed cost analyses.	process can be integrated with purification process and effort can be made to reduce the overall cost of production and transportation due to lower feedstock cost.

readiness level and the commercial readiness index of hydrogen are discussed. Reviews along with discussions thus could be used as a guideline by policymakers, researchers, and scientists for shaping future of hydrogen. Hence, the novelty for this study is to identify and report the efficient thermochemical and electrochemical hydrogen production processes, their storage, CCUS, and applications which would define the future fuel/energy mix for cleaner energy production.

2. Hydrogen as key driver for global GHG emission reduction

The global economic status by 2050 has been predicted to observe rapid growth of development [62] that will demand extensive use of energy [63] in each of the respective emerging and established sectors. In the Paris agreement , 196 signatory countries pledged to decrease the greenhouse gas emissions to bring down the global warming to the pre-industrial level [64]. In addition to that, the commitment by the G20 nations to reduce the CO_2 emissions has accelerated the research and development in the field of hydrogen production, storage, transmission, and distribution. As per the current continual increase in energy-related CO_2-e (carbon dioxide equivalent) greenhouse gas (GHG) emission, global temperature rise has been projected to increase by 3-6 °C above that of pre-industrial era by 2050 [65,66]. Necessity of an efficient global effort has been identified by the intergovernmental panel on climate change (IPCC) to keep the global warming related risks under control [65,67-69]. Based on techno-economic analyses and implementation of various activities to curb the GHG emission, thus checking the global warming effect, the current goal is to reduce overall GHG emission level as low as possible to maintain the global warming temperature rise up to 1.5 °C by 2050 in comparison to that of pre-industrial level [65]. Though ambitious and challenging [33,70,71], an overall shift of technological dependencies from direct combustion of fossil fuels for energy production and implementation of strict regulations to check the overall CO_2-e emission are required to limit the global warming potential (GWP) [72] of the emitted pollutants. The real concern for better environment that can offer sustainable living on earth for human being has motivated the global attention towards producing cleaner energy alternatives like decarbonised hydrogen fuel, renewables (e.g., wind, hydro, and solar electricity) for energy production. Recently, the world has become aware of the quality of the air for breathing and extent of emission related pollution [73]. As a result, strict air pollution regulations have been introducing gradually and attention has been shifting to look for alternative cleaner fuels like hydrogen (H_2) for engines [73-75]. Hydrogen is deemed as a prospective future paradigm shift for renewable energy supply, which can play a most important role for low-carbon economics alongside electricity [22]. Since it has been identified that there requires a rapid progress and implementation of action plans over the next 3 decades to decarbonise the global energy supply system to achieve net-zero emissions (NZE) goals [63,76] by improving efficient energy intensity, changing behaviour of energy uses, producing highly efficient renewable energies, carbon neutral hydrogen and hydrogen-based fuels, expansion of sustainable bioenergy, and efficient carbon capture and sequestration processes, this article focuses on reviewing the currently established and prospective hydrogen production processes.

Hydrogen is lighter than air and readily disperses (liquid density: 70.8 kg/m^3 at standard boiling point and 1 atm, vapour density: 0.08376 kg/m^3 at 20°C and 1 atm) [77]. It is also termed as an efficient energy carrier instead of considering it as a source of energy due to its versatility of production processes and sources (i.e., natural gas, heavy and light hydrocarbon oils, coal, solar, wind, geothermal, biomass, biofuels, nuclear, and electricity) [22,74,78]. When used as fuel, the calorific value of hydrogen (120-142 MJ/kg) indicates the best possible energy-to-weight ratio in comparison to any other fuels [77,79]. Fig. 1 shows that only the radioactive material Uranium has a higher calorific value than hydrogen, and the former is a fuel for nuclear plants rather than for transportation [79,80]. As per the current continual increase in energy-related CO_2-e (carbon dioxide equivalent) emissions to meet rapid projected economic advances by 2050, global temperature rise has been projected to increase by 3-6°C above that of the pre-industrial era [65,66]. The Intergovernmental Panel on Climate Change (IPCC) has recognized the requirements for combined and efficient global efforts to tackle such temperature rises and emission reduction from all possible sectors [65,67-69]. Based on techno-economic development and implementation of various activities to curb the GHG emissions and their global warming effects, the current goal is to reduce the overall emission level as low as possible to maintain the global warming temperature rise at no more than 1.5°C by 2050 in comparison to that of the pre-industrial level [65]. Though ambitious and challenging [33,70,71], shifting technological dependencies on using direct combustion of fossil fuels for energy production, implementing regulations to strictly check the overall CO_2-e emissions to limit the global warming potential (GWP) [72] of the emitted pollutants, and an overall concern for cleaner air for the comfort of living on earth can inspire all of humanity to focus on producing cleaner alternatives like hydrogen fuel, and wind or solar electricity. Recently, the world has become aware of the quality of the air for breathing and the extent of emissions related pollution. As a result, strict air pollution regulations have been introducing gradually and attention has been shifting to look for alternative cleaner fuels like hydrogen for engines [74]. Ugurlu and Oztuna [81] have reported that, when liquid hydrogen (LH_2) was used as fuel in the fuel cell vehicles (FCVs), spark ignition hybrid electrical vehicles (SI HEVs) and spark ignition internal combustion engine vehicles (SI ICEVs), the FCVs efficiently reduced the emissions by 35.1% and 49.6% in comparison to that of SI HEVs and SI ICEVs respectively. Production of hydrogen gas and its application as fuel for the FCEVs has the possibility to decrease overall worldwide greenhouse gas emissions (GHGs) by 50%, which will effectively reduce the demand for petroleum for internal combustion engines by 90% approximately [82].

With supporting instances of reducing significant amounts of global emissions due to the increasing application of natural gas as an alternative to use of fossil fuels like coal and crude oil alongside the emergence since 2010 of renewable as well as nuclear energy resources [31], hydrogen has more opportunity to reduce emissions from hard to abate sectors [30]. Hydrogen has the potential to be utilised as fuel for internal combustion engines in both the gaseous [83] and liquid [84] forms that can effectively help in reducing the emissions of greenhouse gases (GHGs) [85]. It has potential to be used as a dual fuel with methane (i.e., compressed natural gas, CNG) [86] or with petroleum [83,87] as well. The earlier instances of using liquid hydrogen (LH_2) in the space transportation field were the Apollo , the Voyager, the Skylab space station, and the Viking projects [85]. Another environmentally friendly option is to use the hydrogen to produce electricity through fuel cells for vehicle operation, known as hydrogen fuel cell vehicles (HFCVs), which can reduce the overall fossil fuel consumption along with ceasing the vehicular emissions [80,88,89]. The hydrogen-air mixture can be ignited and may resemble a torch that is forced in one direction by the pressure [78]. Due to significant expenditure on technology adoption, fire hazard, storage, transportation and delivery challenges along with

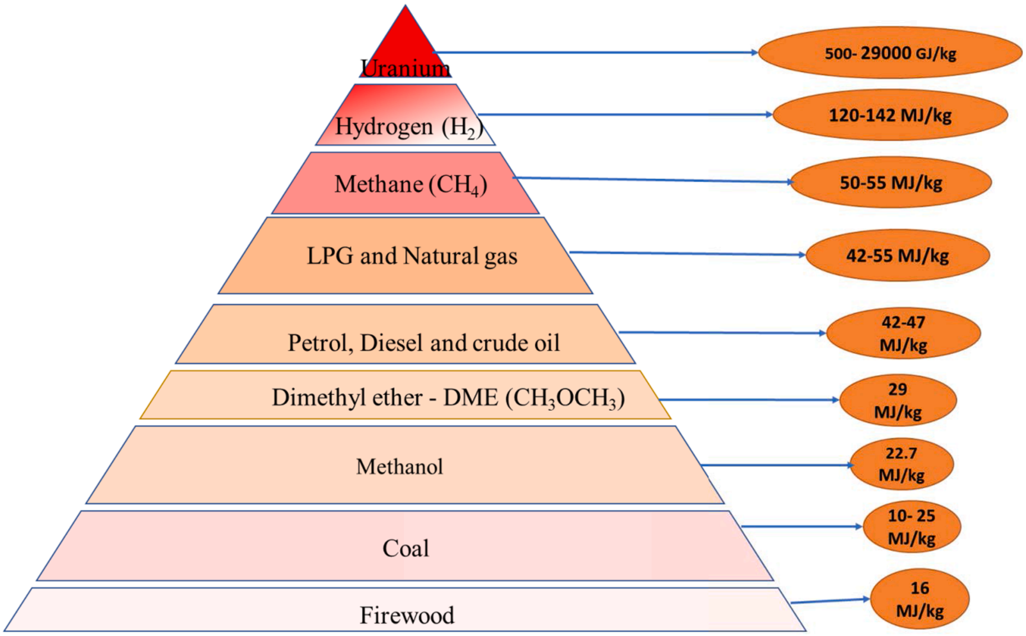


Fig. 1. Calorific values of conventional fuels [79].

lower engine efficiency (20-25%), hydrogen needs to overcome these challenges with economic technical advancement to become the leading cleaner combustion fuel for vehicles in the next three decades [80].

Hydrogen is not a new commodity for some industries, rather it has been effectively in use for more than 50 years in industries for which relevant practices for design of experiments, codes, legislations, and specifications have been established to ensure safe use and applications [78]. Since the fuels are containing energy in its inherent structures, these can be lethal if handled improperly. As of 2020, more than 70 million metric tonnes (Mt) of hydrogen were being produced globally every year for industrial applications [90]. The demand for hydrogen by various industries has increased by 3 times over the years since 1975 which has resulted in the production from fossil fuels of a global share of about 6% of natural gas as well as 2% of coal for hydrogen production [30]. Decarbonisation of energy sectors and hard-to-abate sectors like heating, process manufacturing as well as the transport sector (e.g., passenger vehicles, trucks, aviation and shipping) are the key promising activities [28,29,91,92] to achieve the Kyoto protocol objective which has been set as a global strategy for stabilising climate instability by 2050 [93,94]. Also, adoption decarbonisation pathways through both green electricity and green hydrogen (i.e., about 85% of total demand) will require rapid growth of decarbonised electricity production capability should be about 120,000 TWh by 2050, which is about 4.5 time more, within next three decades at an affordable price to lower the total cost of hydrogen lower enough for mass adoption [95]. Deploying the mix of different efficient processes developed over the years will find better acceptability to meet the ever-increasing global demand of hydrogen production as predicted for checking the global warming crisis.

The goal of hydrogen production for energy sector focuses on reducing GHG emission to net-zero level to avoid global warming crisis [65] by creating highly efficient technologies and value chain infrastructures for stable and rapid globalisation [96-98], and bringing down the levelised cost of hydrogen (LCOH) production [21,99] to an affordable level for the consumers for prompt adaptation. The net zero roadmap by International Energy Agency (IEA) [63] indicates that decarbonisation of the global economy within 2050 will need more than 400 milestones to accomplish a complete transformation of global energy system. Among these the massive reduction of fossil fuel consumption without CCUS integration in every energy consuming sectors, focusing on increased renewable and net-zero energy production, and cleaner hydrogen production. At this moment hydrogen is counted as omnicompetent substance that can be used as source of energy production and raw materials for emission reduction in the industrial production processes. Thus, with a production forecast of more than 500 M tonnes of hydrogen by 2050 has a vast opportunity to meet the gap between the overall energy demand and that of supplied from cleaner electrical and sustainable net-zero bioenergy cumulatively [63,100]. The total energy mix for net-zero-emissions (NZE) scenario predicts that there will be a huge reduction of fossil fuel (i.e., Coal, Oil, and Natural Gas) consumption in 2050 than that of the year 2020 [63]. As per NZE, coal, oil, and natural gas demand will reduce from 5250 Mtce (million tonnes of coal equivalent), 88 Mb/d (million barrels per day), and 4300 bcm (billion cubic metres) in 2020 to 600 Mtce, 24 Mb/d, and 1750 bcm in 2050, respectively [63]. In order to make the best use of these fossil resources, the relevant techno-economic challenges should be tackled within the transition period of energy mixes [101] where the renewable energies will be easily available to consumers at an affordable cost.

3. Global hydrogen production scenario

As shown in Fig. 2a, around 88 Mt of hydrogen was produced globally in 2020 which is 23% more than that in 2015. The global production of hydrogen, refineries, ammonia, and others are shown in Fig. 2a. The production of hydrogen has been increasing every year since 1975 as presented in Fig. 2a. The PwC has projected hydrogen demand and analysed the demand until year 2050. They found that the demand of will grow with moderate and steady pace until 2030 and then demand will grow stronger from 2035 and onward (Fig. 2b). They also surmised that the cost of production will also decrease by 50% during 2030 and further reduction is predicted in 2050 [62]. Hydrogen is produced using different energy sources and technologies and subsequent sections elaborate on the details of the different source. Data from different sources revealed that energy from fossil fuel dominate the production of hydrogen. The availability and the reduction of electricity production cost from renewable energy source pave the way to produce green hydrogen.

Future prospects of hydrogen fuel for various energy applications are very promising in the long-term [102]. Currently about 10 countries (United States of America, United Kingdom , Australia, Canada, France,

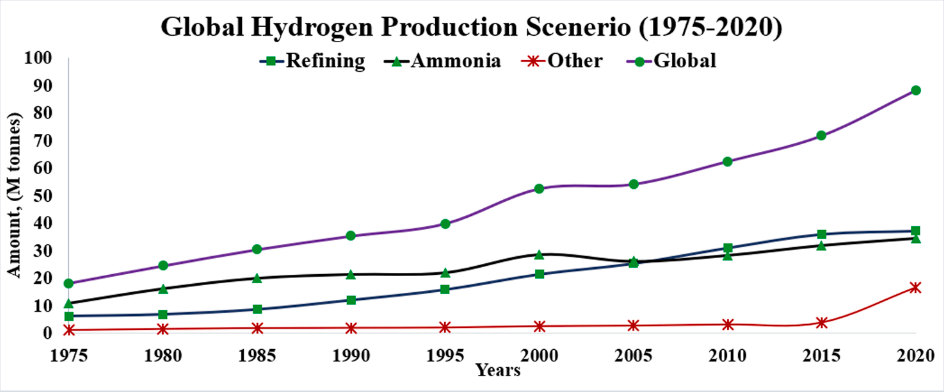


Fig. 2a. Global hydrogen production data between 1975 and 2020 [30].

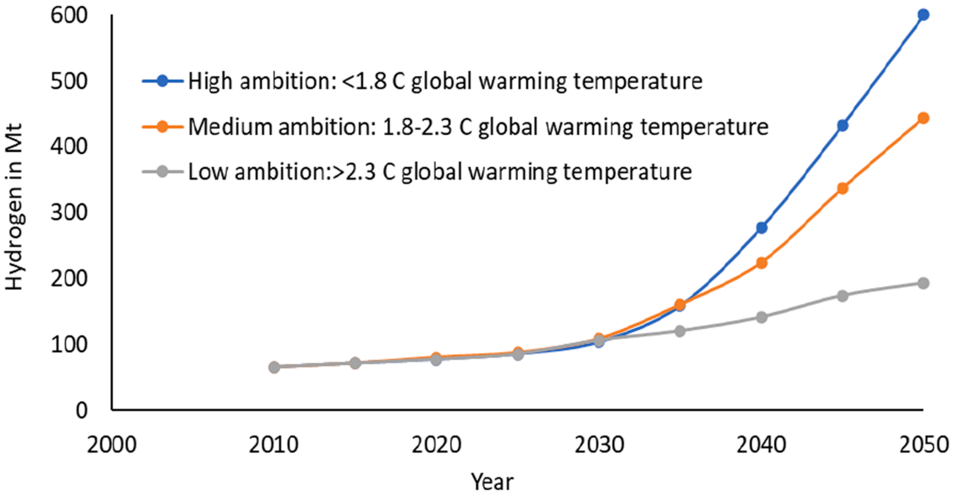


Fig. 2b. Yearly Hydrogen demand to reduce global warming temperature rise [62]

Germany, China, Japan, Norway, and South Korea) around the globe are moving ahead with establishment of their green hydrogen economy [103]. A recent hydrogen roadmap report in the USA [104] has projected that the demand for hydrogen fuel across sectors can rise from 1% to 14% of the total final energy share between 2030 and 2050. The roadmap [104] has divided the technology enabling period between 2020 and 2050 into four categories, namely (a) Intermediate next steps (2020-2022), (b) Early scale-up (2023-2025), (c) Diversification (2026-2030), and (d) Broad rollout (2031-2050). The hydrogen strategy published by the Office of Fossil Energy (FE) of the United States Department of Energy (USDOE) has stated that the transition to the lower or near zero carbon emissions based energy economy will be possible with

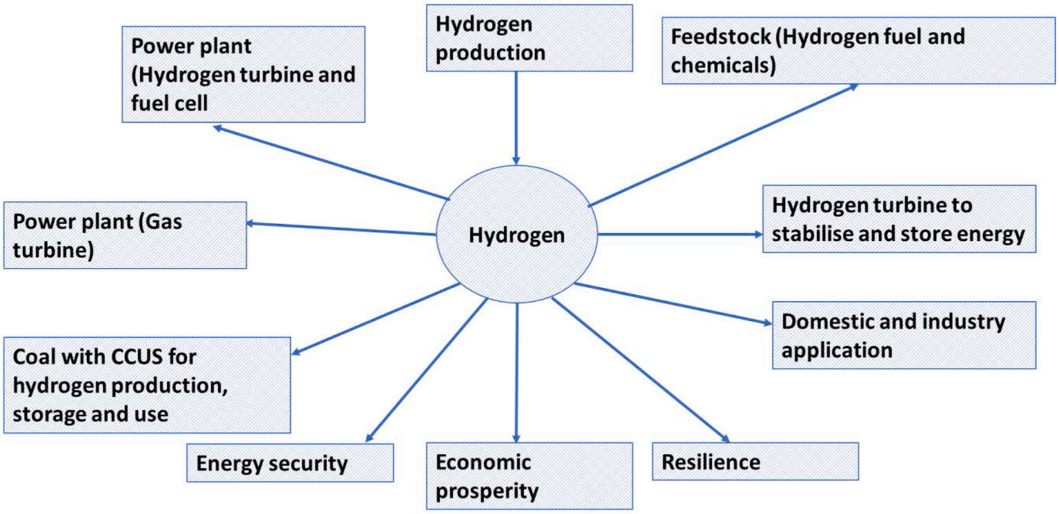


Fig. 3. Integration of hydrogen production streams and applications across sectors for US economic growth, redrawn from ref [105].

the integration of efficient strategies, research and development (R&D) projects, and technology deployment [105]. Fig. 3 shows how the hydrogen strategy can bring benefits by integrating widespread actions over existing fossil fuel-based energy applications. Based on the sources, production processes, emissions capture or reduction and the way the hydrogen economy can offer benefits to the clean energy and environmental value chains, various colours are used to name the hydrogen [102,106-108].

Fig. 4 briefly features the most frequently categorised and termed hydrogen colours collected from various publications, which shows that the processes which do not have an integrated carbon emissions capture facility need to be integrated to establish the clean hydrogen economy value chain.

4. Feedstocks and production processes of hydrogen

All the fuels and energy sources are used directly or indirectly as feedstock for producing hydrogen in their respective efficient methodologies [111-114]. For instance, the direct use of feedstocks occurs in various thermochemical processes where hydrocarbons (i.e., coal, conventional and unconventional [115] natural gases, and oils), biogas, biomass, biofuels, and waste polymers are used as feedstock to produce hydrogen gas. In contrast, the indirect process is the usage of renewable energies (e.g., hydro energy, solar energy, and wind energy) and non-renewable electricity (e.g., coal, gas, oil or nuclear powered powerplants) to crack or electrolyse water into hydrogen gas. The electrolysis process does not produce any CO_2 while cracking the H_2O molecule, but the other thermochemical processes need additional processes with which to be integrated to remove the CO_2 so as to validly claim to be a completely clean application of hydrogen as an energy carrier or industrial raw material [116,117]. Based on the types of production processes and feedstocks used to produce hydrogen, there are varying amounts of CO_2 emissions, investment and infrastructure requirements [118]. Fig. 5 shows the feedstocks, production processes, distribution methods, and applications of hydrogen. From the figure it can be stated that the key feedstocks for hydrogen generation are natural gas, coal, water, and biomass. The hydrogen is used mainly in transport and power generation, the building and manufacturing industries, and as feedstock in creating chemicals and other products. Hydrogen can be stored as gas, liquid, ammonia, and a liquid organic hydrogen carrier (LOHC). The transmission and distribution methods are pipelines, trucks, and ships based on the state of storage as presented in Fig. 5.

Fig. 6 depicts various types of hydrogen production processes. The major conversion processes are thermochemical, photoconversion, electrolysis, and biological processes which are already used technologies for hydrogen production purposes. Though not new, these technologies need further investigation to optimise their production scalability to use hydrogen as a fuel. So, while applying these existing technologies, the key challenges are to overcome the cost burden, emission capture issues, and to enhance the process efficiency to make the adopted technologies more competitive in terms of the current fuel/energy supply systems. Different hydrogen production processes are elaborated in the subsequent sections and sub-sections.

4.1. Reforming processes

In chemical process industries, the reforming process has long been used to crack the low-quality hydrocarbons and convert them into high-quality hydrocarbons by rearranging the hydrocarbon chain structures. Usually, the low-octane hydrocarbons are converted into the higher-octane number gasolines in the refineries so as to improve the combustion quality of the fuel [122]. Thermal reforming requires high temperatures and pressures to reform the chemical structures at the desired level, whereas the catalytic reforming process uses metallic catalysts like platinum (Pt) at a reduced energy level than that of the thermal reforming process [122,123]. Due to attention towards climate protection and greenhouse gas reduction targets with the cleaner energy resources, the reforming process has received much attention to produce hydrogen from cracking the lighter hydrocarbons like natural gas, gaseous hydrocarbons, methanol, ethanol, naphtha, coal, and liquid hydrocarbons which can be used as feedstocks [112,123-125]. The following sections explain the different types of reforming processes for

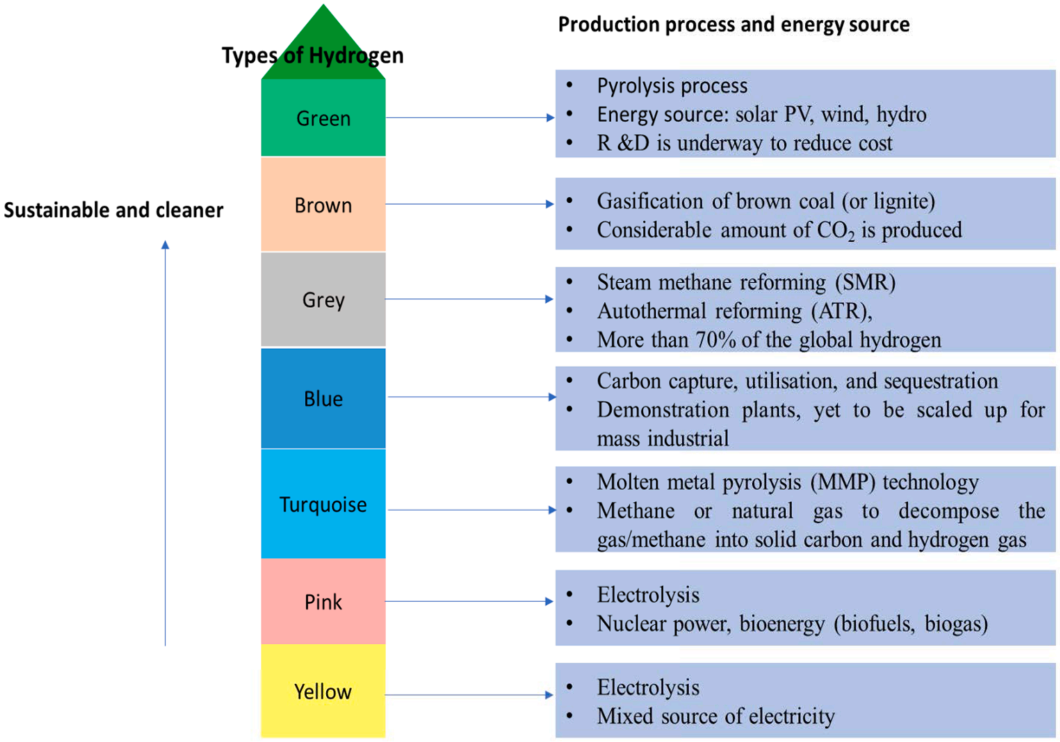


Fig. 4. Different types of hydrogen based on energy source [102,106-110].

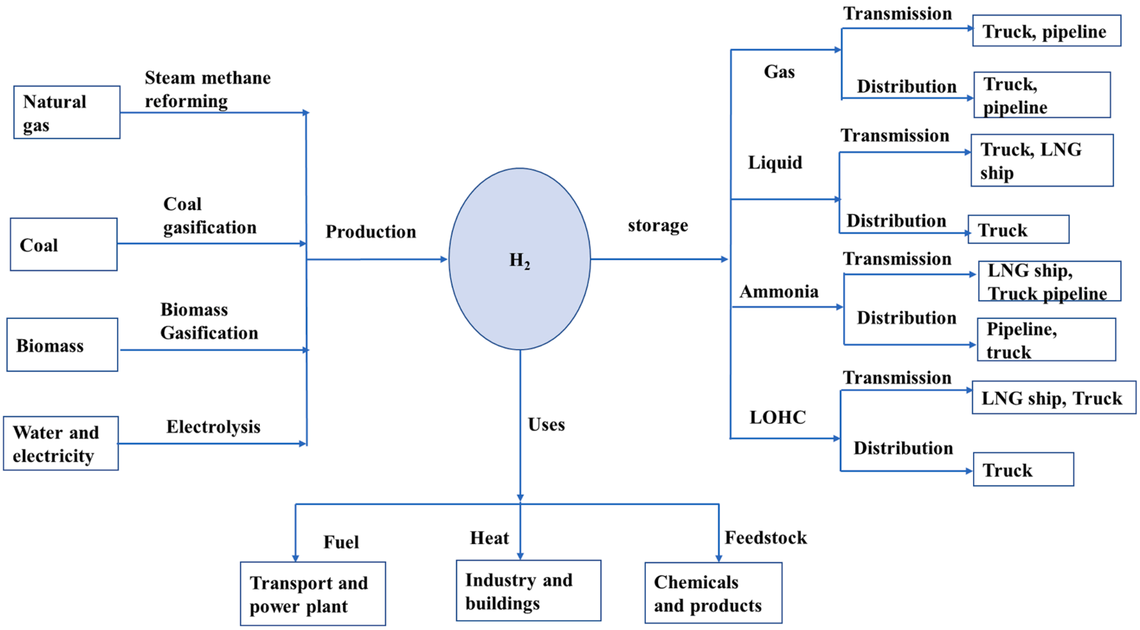


Fig. 5. Feedstocks, production processes, distribution, and applications of hydrogen, redrawn from ref [119].

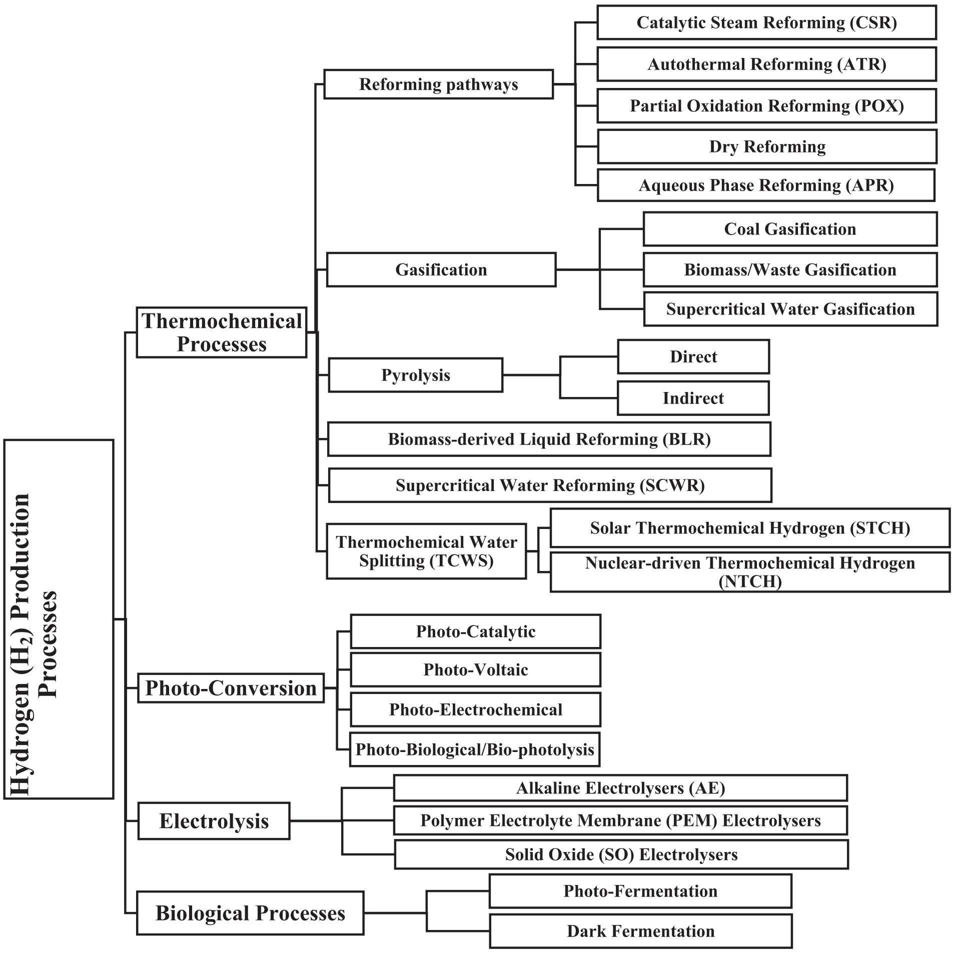


Fig. 6. Types of hydrogen production processes [114,120,121].

production of hydrogen that efficiently utilise different types of feedstocks.

4.1.1. *Steam reforming (SR)*

In the steam reforming (SR) process, steam is used at high temperatures and pressures to crack the organic compounds, which are used as feedstocks, in presence or absence of catalysts to yield hydrogen (H_2) enriched syngas (i.e., mixture of carbon monoxide and hydrogen [126]) [127]. The SR reactors can be operated at a steady-state condition for longer periods with highly efficient (>70% dry basis) amounts of hydrogen production [128]. Multi-stage steam reforming in the presence of optimal temperatures, pressures and a suitable catalyst can increase the yield efficiency [129,130]. Nahar et al. [130] reported 94% yield efficiency of biodiesel steam reforming at 650°C, 10 wt.% Ni/Ce-Zr catalyst, feedstock preheating up to 190°C, molar ratio of steam-and carbon (S/C) of 3 and an operating period of 100 hours for achieving steady state conditions. On the other hand, the SR process of methanol (CH_3OH) can occur between 100-300°C [131,132]. A typical steam reforming reaction process of natural gas (i.e., methane) can occur between 3-25 bar pressure and 700-1000°C in the presence of a suitable catalyst (predominantly Ni-based) [82]. While using natural gas as feedstock, it is crucial to eliminate sulphur (S) found in the natural gas stream to avoid loss of catalytic activities during the SR process [133]. In the non-catalytic SR process, the higher energy input requirement leads to high temperature reactors. For instance, CH_4 cracks into various radicals (e.g., C_2H_4, C_2H_2, and C) at 1000°C, which undergo further cracking at over 1500°C to produce H_2 gas [134]. To determine the optimal design pathway with a feedstock and various variables, multi-criteria decision analysis (MCDA) with analytic hierarchy process (AHP) can make good help. For instance, Janošovský et al. [135] conducted analysis with natural gas and biogas as feedstock options for steam reforming on the basis of criteria like economics, material and energy utilisation, inherent safety and environmental effect. The decision-making hierarchical analysis (about 9027 scenarios) shows that natural gas turns into a good selection when economics, material and energy utilisation are dominant criteria, and the biogas turns into a favourable feedstock when inherent safety is dominant. Hence, the further sub-criteria need to be carefully selected to avoid any biased error in the analyses.

The reactions in the water-gas shift (WGS) method are performed following the steam reforming to use the CO portion of the syngas to dissociate water (H_2O) molecules and maximise the overall hydrogen gas production [136]. CO is reduced into CO_2 while producing H_2 in the WGS process. For efficient WGS process output, the syngas (H_2/CO) content should have a high hydrogen to carbon monoxide (CO) ratio (>3), whereas the carbon dioxide (CO_2) from the syngas can be removed along with the CO_2 produced in the WGS process [81,136]. Indeed, the famous Haber-Bosch process uses this WGS process to produce hydrogen since 1913 [137]. Such a combination of two different reaction processes (i.e., SR and WGS) has increased the interest on hydrogen production from various hydrocarbon compounds for the purpose of producing carbon free energy. One of the key challenges of these processes is the emission of CO_2, which is a harmful greenhouse gas component but a major adopted process of producing hydrogen [81]. Steam reforming is an extremely endothermic reaction, however the WGS process is exothermic [127]. Hence, the SR process is conducted in an adiabatic reactor to avoid high temperature effects on catalysts of the WGS reactors [137]. WGS reactions are conducted in two stages in the typical industrial process, namely low temperature (LT)–CO and high temperature (HT)–CO shift reactions. These multistage reaction processes, in the presence of Fe-based or Cu-based catalysts, can convert more than 99.5% CO into CO_2, thus increasing the concentration of H_2 in the final product line [137]. To maximise the hydrogen production, most industries adopt both the HT-CO and LT-CO shift reactions [138]. Due to the exothermic nature the HT-CO shift reaction, which generally occurs above 350°C, it is executed very rapidly but is unable to convert all the CO. The rest of the CO (usually <10%) is then converted into CO_2 by the LT-CO synthesis at about 180-250°C [137,138]. The generalised steam reforming reaction of oxygenated hydrocarbons and non-oxygenated hydrocarbon compounds [130] are presented in Eqns. 1-3.

Step 1: SR of oxygenated hydrocarbon compounds:

$$C_xH_yO_z + (x-z)H_2O(+heat) \rightarrow xCO + (x + y/2 - z)H_2 \tag{1}$$

SR of non-oxygenated hydrocarbon compounds:

$$C_xH_y + (x-z)H_2O(+heat) \rightarrow xCO + (x + y/2)H_2 \tag{2}$$

Step 2: Converting carbon monoxide (CO) into carbon dioxide (CO_2) by the WGS process.

$$CO + H_2O(-heat) \rightarrow CO_2 + H_2 \tag{3}$$

In the case of converting methane (CH_4) gas by the SR process [139], the reaction steps are presented in Eqns. 4-5.

$$SteamReforming(SR) : CH_4 + H_2O + 206.1\left(\frac{kJ}{mol}\right) \rightarrow CO + 3H_2 \tag{4}$$

$$Water - gasshift(WGS) : CO + H_2O - 41.2\left(\frac{kJ}{mol}\right) \rightarrow CO_2 + H_2 \tag{5}$$

Steam reforming (SR) of ethanol (C_2H_2OH) is presented in Eqns. 6-7 [140].

$$SteamReforming(SR) : C_2H_5OH + H_2O + 255.54\left(\frac{kJ}{mol}\right) \rightarrow 2CO + 4H_2 \tag{6}$$

$$Water - gasshift(WGS) : CO + H_2O - 41.2\left(\frac{kJ}{mol}\right) \rightarrow CO_2 + H_2 \tag{7}$$

The reforming process of ethanol can happen in two stages, i.e., ethanol decomposed into methane that is reformed further. While the reforming reaction of ethanol occurs, higher rate of hydrogen production can be disturbed by a large number of auxiliary reactions if the reactions are not guided with the help of efficient catalysts as per the objective of the reactions [141]. Liu et at. [141] demonstrated that 15Ni-HCa (15 wt.% Ni catalyst with hydrocalumite) catalyst can convert about 99 wt.% of total ethanol into H_2 (86 wt.%) and CO (7 wt.%) at 650 °C. On the other hand, 6% NiO/NaF catalyst can demonstrate about 94% methanol conversion into 100% H_2 under 450 °C [142]. NiO/NaF has very high-level recyclability and low-cost consumption is observed to contain the catalyst. Also, the bio-oil can be converted into 1.49 Nm^3/kg of hydrogen with CaO catalyst (at 650 °C, S/C 2, and Ca/C = 1) [143].

The SR reaction accompanied with WGS contributes about 48% and 30% of the total global quantity of hydrogen production by using natural gas and petroleum oils, respectively [81,129,144]. Also, the coal gasification process and electrolysis processes are used to produce 18% and 3.9% of the total hydrogen in addition to 0.1% contribution from other production processes [81,129]. Natural gas is utilised to generate more than 95% of the total hydrogen in the USA, which makes the production cost greatly reliant upon the gas price [82]. Similarly, countries which are reliant upon coal or hydrocarbons to generate hydrogen for industrial requirements need to consider the price of the feedstock while producing hydrogen. Typical temperature and pressure requirements for the SR process range between 450°C and 925°C, and 290 psig and 500 psig approximately (i.e., 20 to 35 bar) in the presence of suitable catalysts [26,145,146]. SR in the presence of catalysts, known as catalytic steam reforming (CSR), can increase the process efficiency [147]. It is essential to remove the unconverted substances from the reactor because the presence or accumulation of carbon or ashes in the reactor can reduce the activity capacity of catalysts [147]. Part of the reformate is combusted (without forming oxides of nitrogen (NOx) [77,116]) to provide energy in the first step of reaction, and the heat produced in the second step is diverted partly to the process. As a result, thermal efficiency of steam reformers can reach up to 85%-90%. The case of a non-catalytic SR process requires more than 1000°C and it can be uneconomical because methane breaks down at above 1500°C [134]. Bio-oils derived from thermochemical processes contain an aqueous portion for which the CSR process is effective to increase production of H_2 rich gas from the renewable resources like biomass [147,148]. Bio-oil has mainly two fractions, water-soluble (e.g., light weight organics) and insoluble (e.g., lignin-based organics) [148]. Both of these fractions can be separated through water addition [149] or molecular distillation [150] processes. Natural gas, methane, and biogas have been widely used in the CSR process economically, where natural gas has offered better economic outcomes in terms of capital expenditure (CAPEX) and operating expenditure (OPEX) issues [147].

In general, production of 1kg H_2 from natural gas produces about 8.33 kg of CO_2 in the SR-WGS process [144]. Removal of CO and CO_2 are essential for purified hydrogen production from the reforming process. Following the WGS reaction, the methanation, CO_2 absorption in amine solutions, pressure swing adsorption (PSA), membrane separation (MS), and cryogenic distillation (CD) are the most common chemical and scrubbing techniques which are adopted to clean up H_2 from the mixture with CO and CO_2 [128,137]. Among the wide varieties of membranes for separating H_2, the palladium (Pd) and Pd-alloy based metallic membranes have been found as extremely selective to H_2 gas [151]. Though H_2 itself does not emit any GHG pollutants due to combustion for energy production, its production process needs efficient removal of CO_2 during the production processes. Without efficient capture and sequestration of CO_2 from the WGS reactors, the production process will not be defined as a clean fuel production technology.

As a key step to the H_2 production, the energy consumption and pressure input (1-6 MPa) in the multiple stages (HT-CO and LT-CO shift reactions) of the WGS process still faces a risk of incomplete conversion of CO into CO_2. A trace quantity of CO in the H_2 stream in the fuel cell can damage the efficiency very badly [152]. Besides, the economic gains due to the transition from carbonaceous feedstocks to H_2 feedstock for multipurpose applications require that the relevant production processes be economic and efficient. Therefore, an alternative, or a modified WGS process to produce highly purified H_2 at reduced expenses has been a necessity. Electrochemical water–gas shift (EWGS) process (i.e., 25°C, atmospheric pressure) [152] and bio-water-gas shift (BWGS) process (i.e., in the presence of enzymes, anaerobic, 25°C, atmospheric pressure) [153] have been under investigation, which are potentially offering very high purity of H_2 production along with economic gain from the hydrogen value chain. In the EWGS process [152], the oxidation of CO occurs at the anode to produce CO_2.This CO_2 is further oxidised with hydroxide (OH^-) of KOH to produce CO_3^{2-}. At the cathode end, H_2O is reduced to H_2 and OH^-. The K^+ ion from the cathode thus reacts with CO_3^{2-} to produce K_2CO_3. The EWGS reactions may occur like the high temperature polymer electrolyte fuel cell (HT-PEMFC) [154] and an electrochemical pumping is created that helps producing pure hydrogen [154]. The Total EWGS reaction can be presented as shown in Eqns. 8-10.

$$Anode : CO + 4OH^- \rightarrow CO_3^{2-} + 2H_2O + 2e^- \tag{8}$$

$$Cathode : 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{9}$$

$$TotalEWGSreaction : CO + 2OH^- \rightarrow H_2 + CO_3^{2-} \tag{10}$$

Advantages [152] of the EWGS process have been reported as: (i) removal of CO_2 in the form of K_2CO_3, thus producing cleaner H_2 without necessity of CO_2 purification stage; and (ii) application of K_2CO_3 as industrial feedstock in the soap and glass industries as a circular economic contribution. On the other hand [152], oxidation of CO from the SR process can be affected due to its lower solubility to water phase compounds in the anode end. This can be eliminated by increasing concentration of CO in the anode end so that the anode catalysts can help with improving the oxidation process. The increased oxidation of CO in the electrochemical process increases the yield of highly purified H_2 [154]. However, the catalyst quantity needs to be optimised to enhance the process efficiency. To enhance the CO oxidation method, the anode end's catalyst should have weaker interaction with it. Among various metallic compounds, Pt_3Cu has demonstrated efficient activities for increasing the CO oxidation and reduce overpotential of the oxidation process by 0.1V. The $Pt_{2.7}Cu$@CNT catalyst (current density 70 mA/cm^2, catalyst stability period 475 hours) helps optimising the CO adsorption in the anode end and about 99.99% pure H_2 is obtained [152]. That tiny amount of impurity (i.e., 0.01% or 27ppm) is caused by the CO released in the cathode end due to microleakage of the anion exchange membrane (AEM).

The biological way of WGS reaction occurs in the presence of enzymes like carbon monoxide dehydrogenase (CODH) and hydrogenase [138]. These enzymes can contain metallic ions or cofactors like NiFe, which forms complex substances such as NiFe-CODH and NiFe-hydrogenase [138,155,156]. Microorganisms like hydrogenogenic bacteria, methanogenic archaea, acetogenic bacteria, and sulphate-reducer bacteria can ferment the syngas to produce alcohol, methane, hydrogen, or biofuels [138,157-159]. That is why these are also recognised as biocatalysts. In the case of the focus to produce hydrogen from the syngas, the carboxydotrophic hydrogenogenic bacteria can conduct the WGS reaction of CO with H_2O to generate H_2 and CO_2 gases [138,158]. In some cases, biocatalysts offer better effectiveness (i.e., lesser energy consumption, cessation of catalyst poisoning) and advantages (i.e., no influence of H_2:CO in the syngas, reactions can occur at lower temperatures) than that of organic and non-organic chemical catalysts [158]. In a conventional WGS reaction of natural gas, the feedstock is first reformed into CO, H_2 and CO_2 gases. Then the catalytic WGS reactions occur in low temperature shift (LTS) and high temperature shift (HTS) reactors to get higher conversion percentages of H_2 gas from the reformate gas (more than 90%) mixtures [153]. The mixture of H_2 and other gases are passed through a PSA process to collect almost 99.9% pure H_2 gas [153]. On the other hand, the BWGS reaction process is conducted by transferring electrons from the CO to H_2O, which dissociates the H^+ from H_2O and converts into H_2 gas as shown in Eqns. 11-13 [153].

$$\text{Electron transfer from CO} : CO + H_2O \rightarrow CO_2 + 2e^- + 2H^+ ; (CODH) \tag{11}$$

$$\text{Hydrogen gas production} : 2H^+ + 2e^- \rightarrow H_2 ; (hydrogenase) \tag{12}$$

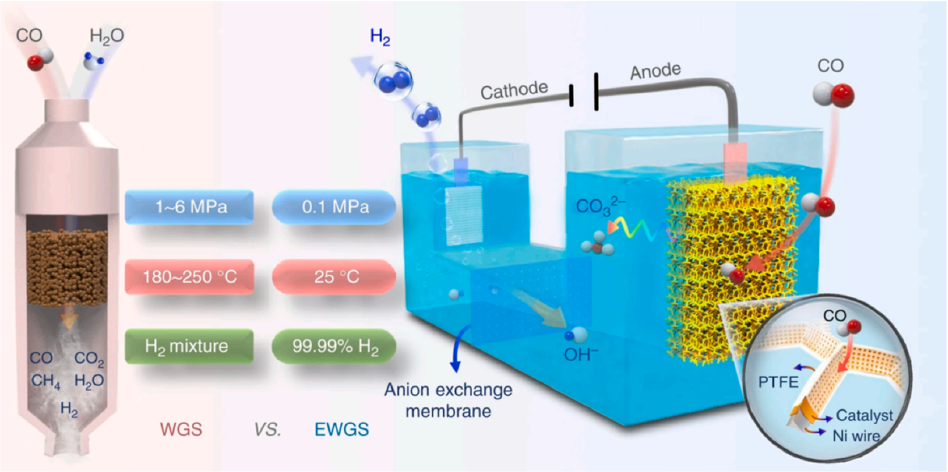
$$\text{Complete BWGS reaction} : CO + H_2O \rightarrow CO_2 + H_2 \tag{13}$$

About 4.46 kcal/mol of energy is produced when the conversion process of CO into CO_2 occurs in an anaerobic environment, whereas the aerobic transformation of CO into CO_2 occurs in the presence of oxygen and the reaction produces about 61.1 kcal/mol of CO conversion [153]. Economic sensitivity analysis is highly recommended to study the benefit of employing the right water-gas-shift reaction process [160-162]. The schematic comparison of WS, EWGS and BWGS is presented in Fig. 7.

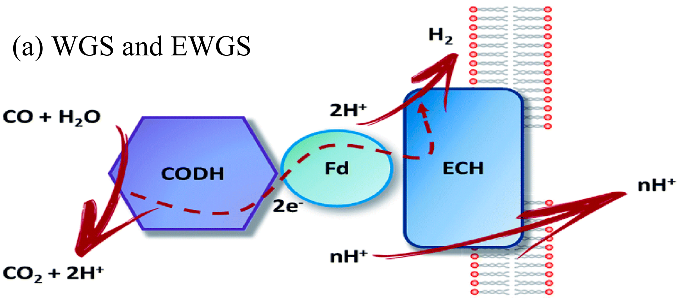
The specification and different types of catalysts used for the SR processes are presented in Table 2.

The temperature and a sufficient supply of steam in comparison to feedstock (e.g., H_2O/C_2H_2OH ratio) in the SR process play a significant role to optimise the hydrogen production. Though the temperature of the SR process can vary from 400-2000 K, the H_2O/C_2H_2OH ratio (between 3 and 6) yields optimum production of hydrogen at 900 K and 1 atm pressure [164]. Change of reaction pressure condition does not have significant effect when the target is to produce hydrogen from complete breakdown of the feedstock [164]. If the reaction conditions are not set well, ethanol can be thermally decomposed into various other organic compounds like ethylene (C_2H_4), acetone (CH_3COCH_3), methane (CH_4), and black carbon (C) at various stages while yielding H_2 in an uneconomic way. Fig. 8 shows pathways for thermal decomposition options of C_2H_2OH in the presence of platinum (Pt) catalyst at lower temperatures (around 300°C and 1 atm), which has been explained by Sutton et al. [165]. Inefficient catalyst selection and dosage rate lead mainly to formation of carbon in both SR and WGS reactions [164]. Fig. 9(a) shows the influence of the H_2O/C_2H_2OH ratio and reaction temperature on hydrogen production efficiency from C_2H_2OH, whereas the loading effect of catalyst in the case of the formation of coke in the SR process is presented in Fig. 9(b) [164].

Use of effective catalysts is required to conduct efficient SR reaction



(a) WGS and EWGS



(b) BWGS

Fig. 7. Schematic comparison between (a) WGS, EWGS and (b) BWGS [138,152].

of the feedstocks used for reforming. The key objectives of using catalysts in the SR reactions are assuring optimal H_2/CO ratio and the ratio of steam and carbon (S/C) [139,140,166], reducing process energy consumption [129,130,134,167], and increasing process efficiency [167,168]. While the catalyst selectiveness, thermal stability, impact of pressure in the reaction chamber, reusability, conversion efficiency, turnover frequency, and avoidance of reduction of catalytic effectiveness because of formation of coke inside the reactor are the key challenges to optimise the reaction process for feedstocks like natural gas, fossil fuel, and alcohol [166,169-172]. The coke formation and catalytic efficiency loss can be eliminated significantly with an optimal S/C ratio [166]. While qualities (i.e., chemical, thermal, and physical) are essential, the cost involvement also influences selecting and continuous development of various types of catalysts [168]. Noble transition materials and non-precious materials are actively used as catalysts, where the precious materials are more expensive than the non-precious ones [166,173-175]. Nickel (Ni), iron (Fe), cobalt (Co), copper (Cu), manganese (Mn), chromium (Cr), silver (Ag), titanium (Ti), gold (Au), molybdenum (Mo), palladium (Pd), platinum (Pt), tungsten (W), rhenium (Re) , osmium (Os),iridium (Ir), rhodium (Rh), and ruthenium (Ru) are the renowned active noble and non-noble active materials which are used as the catalyst or component for composite or multi-metallic catalysts to conduct reaction processes efficiently [166,173,176,177]. Use of an appropriate catalyst support or promotor (directly or indirectly) demonstrates significant improvement in the reactions, i.e., reduction of coke and by-products formation, increased selectivity of the reactants to produce higher yield of hydrogen and stability of the catalysts [166,177]. So, preparing and activating the catalysts with appropriate catalyst supporter for reforming of certain feedstocks is one of the key steps before the reforming process begins.

4.1.2. *Drying reforming (DR)*

In the DR process, there are two reactants (i.e., CO_2 and CH_4) which react to generate synthesis gas (CO and H_2) between 700°C and 900 °C [127], but the reverse water gas shift (RWGS) reactions are favoured beyond 800 °C [178]. This is one of the sustainably promising thermos-catalytical processes as it is very favourable for both industrial and environmental effects. Key challenges have been reported as the deactivation of catalytic performances, and lower H_2/CO ratio (<1) [178]. The DR process can be considered as stoichiometrically similar to that of the biogas production process. The biogas reaction process comprises a ratio of 1:1–1.5 of CO_2 and CH_4, which is near to the stoichiometry of this chemical reaction [127]. Dry reforming of methane (DRM) has been always followed by another four side reactions including the Boudouard reaction, reverse water–gas shift (RWGS) reaction, methane cracking, or CO reduction.

The dry reforming (DR), Boudouard, and RWGS reactions are shown in the Eqns. 14-a, 14-b and 14-c, respectively.

$$DRreaction : CH_4 + co_2 \leftrightarrow 2H_2 + 2CO; (\Delta H = 247kJ/mol) \tag{14-a}$$

$$Boudouard\ reaction :\ 2CO \leftrightarrow CO_2 + C_{(s)};\ (\Delta H = -172\,kJ/mol) \tag{14-b}$$

$$RWGS\ reaction :\ \ CO_2 + H_2 \leftrightarrow H_2O + CO;\ (\Delta H = 41\,kJ/mol) \tag{14-c}$$

The total efficiency of the method is affected by the reduction of efficiency of the catalysts. Therefore, highly sustainable and active catalyst is required to perform the desired reaction activities of the process [127,179]. Table 3 presents the detailed operating specifications of various catalysts for DR of Methane and CO_2 to produce CH_4. [127,179]. Higher catalytic activities have been reported for noble metallic catalysts (i.e., Ru, Pt, Pd)) for the DR process [178]. Ballarini et al. [180] used several materials like K-L Zeolite, K-Al_2O_3, K-Mg/Al oxides, and MgO along with Pt-based catalyst as support for dry reforming of CH_4, for which there were higher stability in the reaction activities to produce hydrogen from methane. MgO/Pt demonstrated higher activity with maximum yield of H_2/CO as 0.73. On the other

Table 2
Catalysts used in SR reaction processes conducted in membrane reactors [163].

Process	Catalyst and catalytic properties	Reaction conditions	Type of membrane reactor
MSR	$Cu/ZnO/Al_2O_3$ (Commercial), MDC-3, G66B (CuO 31~38%, ZnO 41~60%, Al_2O_3 9~21%)	T = 350 °C, P = 6~15 atm, $H_2O/CH_3OH = 1.2$, WHSV = 1 hr^{-1}	Double-jacketed supported Pd
	$Cu/ZnO/Al_2O_3$ (Commercial) modified with ZrO_2 (4.5~25.5 g, and 0.5 mm particle diameter)	T = 250~300 °C, P = 1~5 bar, $H_2O/CH_3OH = 1:1$	Packed-bed reactor (single-fibre) with $Pd–Ag/Al_2O_3$
	Cu-based - Cu/Zn/Mg (commercial)	T = 300°C, P = 1.5~3.5 bar, $H_2O/$ $CH_3OH = 3:1$, WHSV = 0.36~1.82 hr^{-1}	Dense Pd-Ag*
	CuO (64%) + Al_2O_3 (10%) + ZnO (24%) + MgO (2%)	T = 350 °C, P = 1.3 bar, $H_2O/CH_3OH = 6:1$, l/ $l/_{cat} = 3g$	Dense Pd-Ag*
	$LaNi_{0.95}Co_{0.05}O_3/Al_2O_3$ (co-precipitation method, Alumina as binder)	T = 400 °C, P = 0.05 bar	Pd-Ag CMR
	$CuO/ZnO/Al_2O_3$ (Commercial)	T = 310 °C	Pd
	Ru (5 wt.%)-Al_2O_3 (Commercial, 3g)$W_{cat} = 3g$, 5 wt% Ru	T = 400 °C, P = 1.3 bar	Pd-Ag supported and dense
	$CuO/ZnO/Al_2O_3$ (Commercial) (G66MR, 250–355 μm particle size)	T = 200 °C, P= 1 bar	Carbon molecular sieve
	$ZnO/CuO/$ Al_2O_3 (Commercial)	T = 200~260 °C, P = 1.2 bar, H_2O $/CH_3OH = 1.3$	Dense $Pd-Ag_{20\%}$*
ESR	Ni (25 wt.%)/ZrO_2 and Co (15 wt.%)/Al_2O_3 (Commercial)	T = 400 °C, P = 8–12 bar, GHSV = 800–3200 h^{-1}	Pd/PSS composite
	Ru (5 wt.%)/Al_2O_3 (Commercial, 4~7g, size 1~2 mm)	T = 400~450 °C, P= 1.5~2.0 bar, H_2O: $C_2H_5OH = 8.4$~13.0	Dense Pd–Ag*
	Pt (0.5 wt.%)/Al_2O_3 (Commercial, 6.3g, 2 mm size).NiO (25 wt. %)/SiO_2, (Commercial, 6.0 g, 2 mm size)	T = 400~450 °C, P = 1.5~2.0 bar, H_2O: $C_2H_5OH = 8.4$–13.0	Dense Pd–Ag*
	Rh/SiO_2 and Pt/TiO_2, Degussa P25 for WGS	T = 300–600 °C	Composite Pt/PSS
	MDC-3: $Zn–Cu/Al_2O_3$ (Commercial)	T = 320~450 °C, P = 3~10 atm	Pd–Ag/PSS composite
	Ru (0.5 wt.%)/Al_2O_3 (Commercial, 3 g)	T = 400 °C, $H_2O:C_2H_5OH = 11:1$, GHSV = 2000 h^{-1}	Dense Pd–Ag*
	Pt/Al_2O_3 (7.2 g, 2~3 mm)$W_{cat} =$	T = 400 °C and 450°C, P = 150~200 kPa, H_2O: $C_2H_5OH = 4$, 10 and 13	Dense Pd–Ag*
	Ru (5 wt.%)/$Al_2O_{3,}$ (Commercial. 3g)	T = 400 °C, P = 1.3 bar	Dense Pd–Ag*
	CO (15 wt.%)/Al_2O_3 (Commercial. 3g)	T = 400 °C, P = 3~8 bar	Pd/PSS composite
	Co (15 wt.%) + La (3.1 wt.%), Rh (4 wt.%), (Commercial. 3g, 143m^2 g^{-1}, 150~250 mm)	T = 400 °C, P= 3–8 bar	Dense Pd–Ag
	Na (0.2~2 wt.%)–Co (12.5 wt.%,)/ZnO, (0.45 g, 0.6~0.85 mm)	T = 600~750 °C, P= 7~70 atm, S/C = 3~12, GHSV = 8500~83000 h^{-1}	Silica–alumina composite MR
Acetic acid SR	Ni (4g)and Ru (2g of 5 wt.%), (Commercial)	T = 400~450 °C, P = 1.5~2.5 bar	Dense Pd–Ag*
	Commercial Ni	T = 400 °C, P= 1.5~4.0 bar, $H_2O/CH_3COOH = 10:1$	Pd–Ag dense*
Glycerol SR	Ru (0.5 wt.%)/Al_2O_3 (Commercial, 3g)	T = 400 °C, P= 1.5~4.0 bar, $H_2O/C_3H_8O_3 = 6:1$ WHSV = 0.1~1 h^{-1}	Pd–Ag dense*
Naphtha reforming	Pt (0.3 wt.%) + Re (0.3 wt.%)	T = 505 °C, P = 34~37 bar	Fluidised bed $Pd–Ag_{23\%}$

* SSP = self-supported palladium membrane; T = temperature; S_{BET} = BET specific surface area; P= pressure; WHSV = weight-hourly-space-velocity; GHSV = gas-hourly-space-velocity.

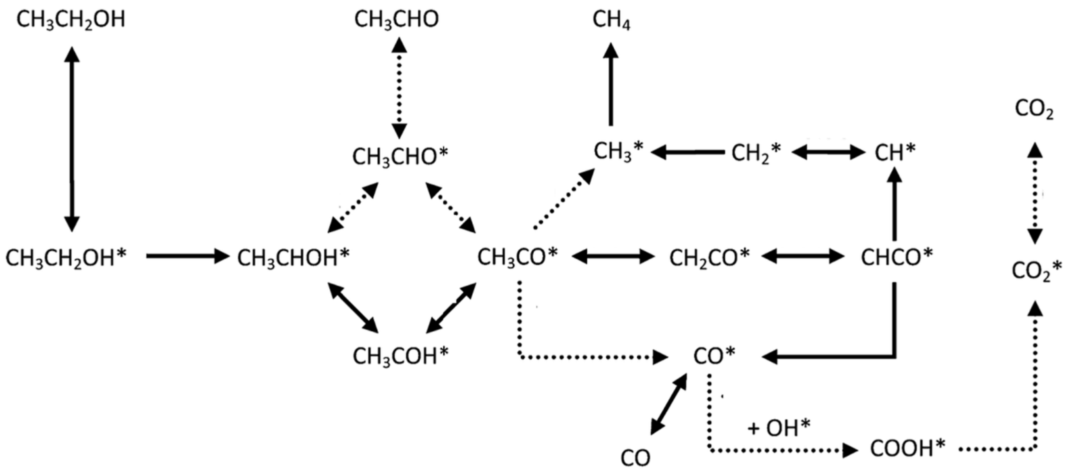
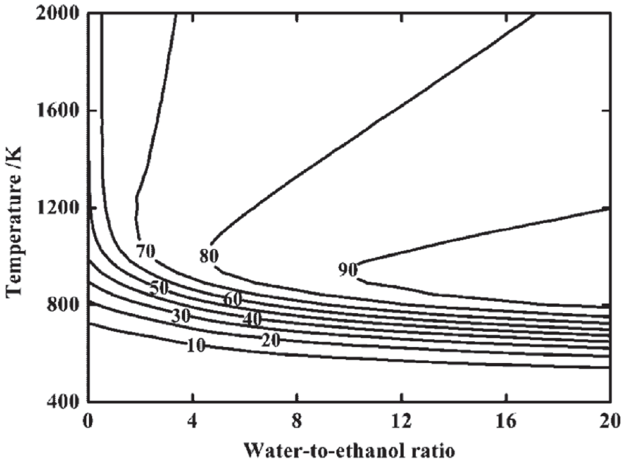
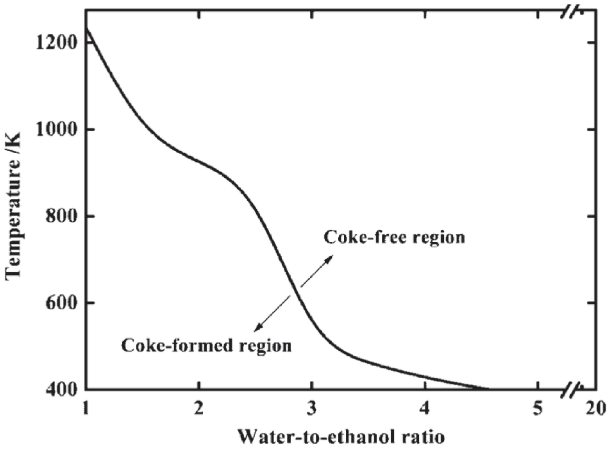


Fig. 8. C_2H_2OH decomposition pathways (dehydrogenation/hydrogenation reactions) in presence of Pt catalyst [165].

hand, Xie et al. [181] reported that the bimetallic catalyst combination of PtCo/CeO2 demonstrates better effectiveness to produce hydrogen and the catalyst itself shows higher resistance to the formation of coke, thus eliminates the risk of deactivation of catalysts. Also, higher temperature and pressure (i.e., 850 °C, 1 MPa) in the DR process with hydrotalcite-derived 100Ni20Ir catalyst has higher methane conversion rate (68.5%) and the catalyst exhibited strong carbon tolerance against the usual catalyst deactivation due to carbon deposition on the catalyst. Hence, the DR process has greater prospect to use either natural gas or biogas which have more methane content to crack into hydrogen. For instance, Hajizadeh et al. [182] reported that at a rate of 48.07 kg/h biogas input to the DR reactor may produce about 8.11 kgH_2/h in presence of $Co-Ni-Al_2O_3$ catalyst. This process was reported to be less expensive counting about US\$1.39/ kgH_2.



(a) T vs H_2O/C_2H_2OH ratio



(b) T vs H_2O/C_2H_2OH ratio

Fig. 9. Effect of reaction temperature (T) and H_2O/C_2H_2OH ratio on: (a) hydrogen production; and (b) coke (Carbon) formation SR reaction process of C_2H_2OH at equilibrium condition [164].

4.1.3. *Partial oxidation (POX)*

Steam reforming (SR) of natural gas, biofuels or various hydrocarbon fuels requires heat energy input to conduct the reaction and produces CO_2. On the contrary, a partial oxidation (POX) reaction produces heat and lesser amounts of CO_2. While comparing with the steam reforming process, 1 mole of methane gas (as natural gas) may produce about 25% less hydrogen by the partial oxidation process. Partial oxidation reformers react the fuel with a sub-stoichiometric quantity of oxygen [128] as shown in Eqns. 15-a and 15-b.

$$\text{Step 1}: CH_4 + 1/2O_2 \rightarrow CO + 2H_2(+\Delta H) \quad (15\text{-a})$$

$$Step2 : WGSreaction : CO + H_2O \rightarrow CO_2 + H_2(+smallamountofheat) \quad (15\text{-b})$$

The reaction process differs from the steam reforming process with the thermodynamic behaviour, i.e., the POX process is exothermic with $H_2/CO=2$, whereas the steam reforming process is highly endothermic (e.g., 206 kJ/mol for steam reforming of 1 mol methane gas) [183]. Following this, pure H_2 is separated usually using a Pressure Swing Adsorption (PSA) technology [184]. About 6% of the total worldwide production of natural gas is accounted for as dedicated raw material for production of hydrogen gas. That accounts about three-fourths of the total hydrogen production globally. The generic POX reaction of hydrocarbon fuels is presented in Eqn.16-a.

$$Generic\ hydrocarbon\ fuel : C_nH_m + (n/2)O_2 \rightarrow nCO + \left(\frac{m}{2}\right)H_2 + heat \quad (16\text{-a})$$

In comparison to that of the catalytic reforming processes, the POX process does not require any catalyst to conduct the reforming process. As a result, this reaction process does not experience the loss of catalytic effectiveness due to coke formation and deposition on catalysts Though catalysts are absent, the key challenging issue of the POX reaction process is the requirement of high temperatures which is more costly than other reactors used. Also, the higher temperature leads to generation of soot and the lower H_2/CO ratio (1:1 to 2:1) for lesser H_2 production from the same amount of feedstock used for the other reforming processes like SR and AR processes, yet the DR process still requires the WGS process to increase the quantity of H_2 production. Besides, the WGS reaction is conducted to convert the hazardous CO gas into CO_2. Generally, the POX process is effective for reforming the heavier hydrocarbons like petrol, diesel, and heavy oils at temperature ranging between 1150 °C and 1315 °C in presence of 600 kPa reactor pressure for efficient reforming to hydrogen [185]. Table 4 shows a comparative study of reforming of methane, methanol, diesel/gasoline, and coal via SR and POX processes and how efficient the chemical processing is. Certainly, the produced hydrogen quantity in the SR method is considerably more than that of the POX method for all these feedstocks [77].

POX reaction for methanol and ethanol can be expresses as in the Eqns. 16-b and 16-c, respectively [186].

$$POXofMethanol : CH_3OH + 1/2O_2 \rightarrow 2H_2 + CO_2 + \left(\Delta H \approx 192.2\frac{kJ}{mol}\right) \quad (16\text{-b})$$

$$POXofEthanol : C_2H_5OH + 3/2O_2 \rightarrow 3H_2 + 2CO_2 + \left(\Delta H \approx 620.3\frac{kJ}{mol}\right) \quad (16\text{-c})$$

[186] Use of catalysts to conduct the POX reactions of methanol and ethanol can improve the temperature management ability and improved hydrogen production rate. Agrell et al. [187] conducted POX reaction of methanol in presence of Cu40Zn60 catalyst at around 185-215 °C for $O_2/CH_3OH = 0.1$, for which the hydrogen production improved significantly at lower temperature [188]. Yang et al. [189] conducted methanol partial oxidation reforming in presence of Au-CuO-ZnO (w/w: 3% Au, 37%Cu, and 60%Zn) catalyst at 523K that produced 97.7% selectivity type hydrogen from the process. Whereas, in case of catalytic partial oxidation of both methanol and ethanol, Hohn and Lin [186] have discussed all the possible and complex reactions pathways that may take place. In presence of h-BN-Pt.Al2O3 catalyst, the partial oxidation of methanol can be started at room temperature, which has been termed as cold start by Chen et al. [190]. The authors reported that hydrogen was generated at a rate of 1.3mol/mol of methanol for $O_2/C=0.7$, and $S/C=1.5$. Still there is no highly recognised catalyst and optimised process parameters reported for the POX reactions to produce hydrogen though addition of catalysts in the POX process has been capable of controlling the temperature changes during reactions to produce hydrogen.

4.1.4. *Autothermal reforming (ATR)/ Oxidative steam reforming (OSR)*

Autothermal steam reforming (ATR) is a combination of both SR (endothermic) and POX (exothermic) reactions through combined input of fuel, steam, and air together into the reactor [128], which can be used to efficiently reform the bio-oil to produce H_2 [191]. Due to generation of heat in the POX method, reforming methods do not require external heating sources in this reaction process, but it is considered as one of the most efficient processes of its kind. Nevertheless, both POX and ATR processes are expensive, and these processes require an intricate oxygen gas separation process from the atmosphere for further reactions. A WGS reaction process is conducted to convert the CO and boost the hydrogen generation policies [184]. Oni et al. [192] have reported that the ATR process along with CCUS process can offer production of blue hydrogen

Table 3
Latest studies on dry reforming of methane [127,179].

Input CH_4/CO_2	Metals	Temperature (°C)	Output H_2/CO	CH_4Conversion (%)	CO_2Conversion (%)	Carbon Formation mg/g-Catalyst
0.5	Ce–Gd–O	800	1.07	50	88	Nr
0.8	Rh–Al	700	1	42	nr	Nr
1	NiCo/$CeZrO_2$	800	0.84	79	84	0.24%–8.2%
1	WC	900	0.96	95	95	None
1	Ni–Al	700	0.67	19	31	Nr
1	Ni–Pb–Al	700	0.88	60	78	Nr
1	Ni–Pb–1P–Al	700	0.77	55	71	Nr
1	Ni	700	1	54	66	41
1	Co	700	1	75	67–80	20–268
1	Ni–Co	700	1	56–71	83	290
1	Pt–Ru	700	<0.5	90	48	Nr
1	La–NiMgAlO	700	0.8	80	85	Nr
1	Ni	750	nr	32	36	3.6% of inlet C
1	Ce–Gd–O	800	0.96	68	72	Nr
1	Pt–Al	900	nr	nr	nr	22% of inlet C
1	Ni–La–Al	950	nr	99	90	Nr
1	NiO–MgO	700	0.87	67	77	Nr
1.5	Ni–Al	750	0.9	49	81	Nr
1.5	Ni–Mg–Al	750	0.86	59	70	Nr
1.5	Ni–La–Mg–Al	750	0.95	61	70	Nr
1.5	Rh–Ni–Mg–Al	750	1	58	85	Nr
1.5	Rh–Ni–La–Mg–Al	750	1.06	50	94	Nr
1.5	Rh–Ni	800	1	65	100	Nr
1.5	Ni–Al	850	0.55	72	96	180
1.5	Ni–Ce–Al	850	0.65	73	97	170
2	Ce–Gd–O	800	0.84	66	46	Nr
2.1	Ni	750	nr	21	29	3.6% of inlet C

Table 4
Steam reforming and POX processes with methane, methanol, gasoline, and coal [77].

Products	Methane		Methanol		Diesel/ Gasoline		Coal	
	SR (%)	POX (%)	SR (%)	POX (%)	SR (%)	POX (%)	SR (%)	POX (%)
H_2	75.7	47.3	71.1	37.8	71.1	37.8	63.1	23.6
N_2	1.9	33.5	1.9	39.8	1.9	39.8	1.9	49.2
CO_2	19.9	16.7	24.5	19.9	24.5	19.9	32.5	24.7
Others	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

at a cost range of \$1.69-\$2.55 per kg. The CO_2 emission from the ATR process (i.e., 3.91 $kgCO_2$.eq/ kg H_2) is very low in comparison to other processes. Cost for emission capture is added to the production expenses, which also affects the feedstock price. Catalyst selection has been effective to the ATR process. For instance, Zhang et al. [193] reported that the addition of Pd-Zn/γ-Al_2O_3 at 400 °C can produce about 45% (v/v) of hydrogen efficiently. It has been observed that the precise thermodynamic analysis of the ATR process of the components of the bio-oils are absent [194]. The ATR reaction process is also termed as the oxidative steam reforming (OSR) process due to its nature of reacting components [195]. The typical reaction process of the ATR or OSR process is shown in Eqn.17.

$$Fuel\left(C_xH_yO_z\right) + air + \text{steam} \rightarrow CO_2 + H_2 + N_2(-\Delta H) \tag{17}$$

While producing hydrogen from various hydrocarbons, the SR, DR, and POX processes generally release CO_2 which needs to be integrated with the carbon capture, utilization, and storage (CCUS) techniques to decarbonise these processes and save the world from the impact of CO_2 emissions. Also, pyrolysis and ATR process combination can solve waste plastics to hydrogen production issues. Cortazar et al. [16] have reported optimised production of hydrogen from several waste plastics (HDPE, PP, PS, PET), mixed plastics, biomass, and HDPE:Biomass (25:75, 50:50, 75:25) waste streams by using pyrolysis and ATR processes in line. Among the liquid streams, the highest hydrogen was reported from PP (64.1%), and HDPE (64%). Also, the lowest yield was from PET (49.4%). Addition of HDPE increased the overall hydrogen production from the plastic/biomass mixed streams. As a result, if these processes are integrated with efficient CCUS process, the levelised cost of hydrogen production can be effectively controlled while resolving the global waste accumulation problems due to poor recycling of waste plastics [192,193].

4.1.5. *Aqueous phase reforming (APR)*

In the aqueous phase reforming (APR), the feedstock (e.g., oxygenated/non-oxygenated hydrocarbons [196]) is treated at lower temperatures in an aqueous solution in a single step without the necessity of vaporising the reactants as required in the steam reforming process to produce hydrogen gas [197]. Usually, this reaction occurs at about 200-250°C temperature and up to 60 bar pressure in the presence of platinum (Pt), tin (Sn), cobalt (Co) or nickel (Ni)-based metallic catalysts in addition to alumina as a catalyst support [196,198-200]. This process is less energy consuming and “greener” than the other reforming processes [196]. This process has a great potential to be considered as one of the economic methods to generate hydrogen gas from organic compounds [198]. When biomass (usually long chain hydrocarbons or polymers) is directly used as feedstock in the hydrogen production process, there are additional complexities in the process implementation due to their variation of composition, sizes, low-energy density, and transportation. To ease these complexities, biomass could be converted into liquid (e.g., ethylene glycol, bio-ethanol, polyols, bio-methanol, bio-oil, cellulose) or gas (e.g., syngas, biogas, methane) as an intermediate raw material to be transported, treated and processed efficiently in the reforming process to produce hydrogen [199,201]. Cortright et al. [197] first demonstrated that, at about 500K temperature, the hydrocarbons having at least 1:1 stoichiometric ratio between C and H molecules can be reformed to generate H_2 and CO_2 gases. The stoichiometric APR reaction of sugar–alcohol sorbitol ($C_6O_6H_{14}$) in the presence of Pt catalyst can be shown as in Eqn. (18) [197]:

$$C_6O_6H_{14}(l) + 6H_2O(l) \leftrightarrow 13H_2(g) + 6CO_2(g) \tag{18}$$

To make the APR process efficient for dedicated hydrogen gas production, it is essential to continuously capture CO_2 from the product side. Otherwise, both the H_2 and CO_2 gases react readily in the presence of the same catalysts at low temperature to produce short chain hydrocarbons like methane (CH_4) as per Eqn. (19).

$$4H_2(g) + CO_2(g) \leftrightarrow CH_4(g) + 2H_2O(g) \tag{19}$$

Though higher hydrogen yield is possible with the APR process, such consumption of hydrogen is undesirable (i.e., series-selectivity challenge) in the hydrogen industry. On the other hand, this hydrogen consumption process can be efficiently employed in the hydrogenation processes in the biorefineries [197,198]. If the catalysts in the APR process possess lower rates of cleaving the C-O bonds, the resulting alkane production rate could be reduced as well [202]. Though Ni-based monometallic catalysts are very common, the Pt-based monometallic catalysts demonstrate better activity as well as selectivity [202] in terms of abating conversion of H_2 into alkanes with further reactions. Moreover, the bimetallic catalysts like PtNi, PdFe, PtFe in addition to PtCo demonstrated better activities in APR processes than that of the monometallic catalysts [202]. Besides, the catalyst supports like TiO_2,CeO_2, C (black and activated carbon), SiO_2, ZrO_2, ZnO, SiO_2-Al_2O_3 and Al_2O_3 can improve the activity of the catalyst [203].

Due to variation of activities and selectivity characteristics, the appropriate catalysts can be determined by following the methodologies depicted in Fig. 10 as presented by Huber and Dumesic [202]. When 10 wt.% aqueous ethylene glycol is reformed at 498K and at 29.4 bar in the APR process in the presence of Pt catalyst and various catalyst supports, then the effectiveness of producing hydrogen gas with the Pt/catalyst supports were obtained as, Pt/TiO_2>Pt-Black carbon>Pt/activated C>Pt/Al_2O_3>Pt/ZrO_2 [203]. Higher amounts of alkane formation can be observed when black carbon is used as the catalyst support. By comparing the hydrogen production capacity with the alkane formation route in the presence of a catalyst system, Pt/Al_2O_3 has shown efficient selectivity for conversion of ethylene glycol to hydrogen via the APR process [203].

4.2. Bio-water-gas shift (BWGS) reaction

The BWGS reaction occurs in the presence of enzymes like hydrogenase and carbon monoxide dehydrogenase (CODH) [138]. Microorganisms like hydrogenogenic bacteria, methanogenic archaea, acetogenic bacteria, and sulphate-reducer bacteria can ferment the syngas to produce alcohol, methane, hydrogen, or biofuels [138,157-159]. That is why these are also recognised as biocatalysts. In the case of the focus being to generate hydrogen from the syngas, the carboxydotrophic hydrogenogenic bacteria can conduct the water gas shift reaction of CO with H_2O to generate H_2 and CO_2 gases [138,158]. In some cases, biocatalysts offer better effectiveness (i.e., lesser energy consumption, cessation of catalyst poisoning) and advantages (i.e., no influence of H_2:CO in the syngas, reactions can occur at lower temperatures) than that of organic and non-organic chemical catalysts [158]. In a conventional WGS reaction of natural gas, the feedstock is first reformed into CO, H_2 and CO_2 gases. Then the catalytic WGS reactions occur in low temperature shift (LTS) and high temperature shift (HTS) reactors to attain higher percentages of H_2 conversion from the reformate gas (more than 90%) mixtures [153]. The mixture of H_2 and other gases are purified through a pressure swing adsorption (PSA) process to collect almost 99.9% pure H_2 gas [153]. The BWGS reaction process is carried out by transferring electrons from the CO to H_2O, which dissociates the H^+ from H_2O and converts into H_2 gas as shown in Eqns. 20-22 [153].

$$\text{Electron transfer from CO}: \ CO + H_2O \rightarrow CO_2 + 2e^- + 2H^+; (CODH) \tag{20}$$

$$\text{Hydrogen gas production}: \ 2H^+ + 2e^- \rightarrow H_2; (hydrogenase) \tag{21}$$

$$\text{Complete BWGS reaction}: \ CO + H_2O \rightarrow CO_2 + H_2 \tag{22}$$

If the conversion of CO into CO_2 occurs in an anaerobic environment, then the reaction yields 4.46 kcal/mol of CO conversion. However, the aerobic transformation of CO into CO_2 occurs in the presence of oxygen and the reaction produces about 61.1 kcal/mol of CO conversion [153]. Economic sensitivity analysis is recommended to examine the benefit of employing the right water-gas-shift reaction process [160-162].

4.3. Biomass pyrolysis

Biomass can easily be converted into secondary energy without investing huge capital and the biomass is mostly available locally [14]. Biomass pyrolysis process is considered as cleaner process to convert

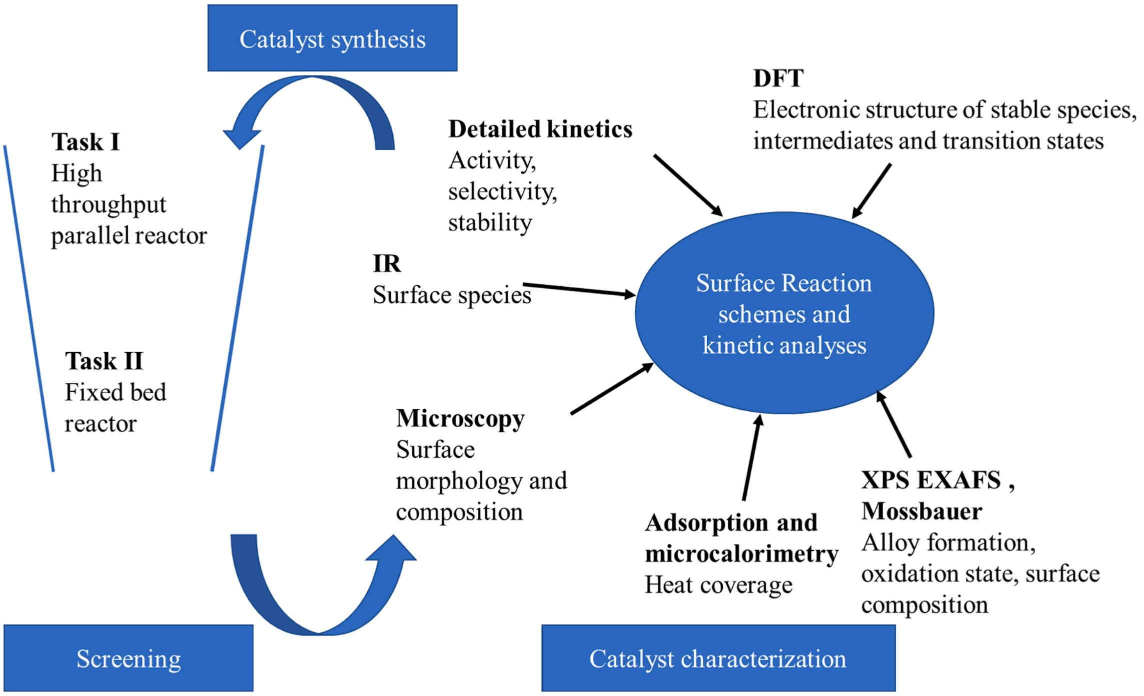


Fig. 10. Methodologies to develop catalysts [202].

biomass and organic waste into secondary energy sources. The biomass pyrolysis process can be integrated in the process of hydrogen production. Aziz et al. [204] reviewed different process to produce hydrogen using the pyrolysis process. The thermal breakdown of lignocellulosic derivatives in an inert condition without oxygen is called pyrolysis [205]. The generation of H_2 from biomass starts with fast pyrolysis of the biomass [206]. In this thermochemical process, biomass feedstock is cracked into charcoal, gases, and liquid (bio-oil or bio-crude), methanol, acetone, and acetic acid by heating the biomass to around 1025K without oxygen [207]. The key products of the biomass pyrolysis process can be presented as in Eqn. (23). In the pyrolysis process, the organic material is decomposed by a thermal process in the absence of oxygen to produce volatile and inorganic elements containing carbonaceous char [208]. Pyrolysis reactions can occur in the presence or absence of catalysts to produce the desired products [209,210]. Çağlar and Demirbaş reported that an increased amount of $ZnCl_2$ catalyst (>17%) in the pyrolysis reaction of biomass like Olive husk produces more hydrogen gas (mixture of H_2 and paraffins > 70%) from the pyrolysis process [207]. Akubo et al. [17] conducted integrated pyrolysis-catalytic steam reforming of biomass feedstocks (hemicellulose (xylan), lignin, and cellulose) and biomass wastes (sugarcane bagasse, wheat straw, palm kernel shell, rice husk, coconut shell, and cotton stalk) that increased the productivity of hydrogen gas in the presence of 10 wt% Ni/Al_2O_3 catalyst. The syngas (mixture of H_2, CO and CO_2) is fed into a pressure swing adsorbent at room temperature to separate the H_2 gas from the gas mixtures. The pyrolysis reaction is presented in Eqn. (23).

$$\text{Pyrolysis reaction}: \; Biomass \rightarrow H_2 + CO_2 + CO + Hydrocarbon\ gases \tag{23}$$

There are four types of biomass feedstocks available in the world: (1) woody plants; (2) herbaceous plants or grasses; (3) aquatic plants; and (4) manures [211]. Biomass feedstocks can be acquired abundantly from diverse sources like the wastes from animals, municipal solid waste streams, food processing industries, rivers or oceans, residual wastes from agriculture, forests and wooden materials [212]. Biomass, being a mixture of various low molecular weight and macromolecular based substances, can be considered one of the key renewable energy resources for fuel production [213-215]. Besides, the available conversion processes (e.g., thermo-catalytic or bio-chemical processes) can efficiently convert these biomass raw materials into gas, liquid or solid commodities (i.e., biomass to chemical/hydrocarbon) which can be further treated to produce a desired fuel stream [216]. Converting biomass into liquified hydrocarbon mixtures offers better volumetric energy density and efficient responses on catalytic processes due to reduction of catalytic poisoning [217]. The bio-oil is typically an intricate mixture of various hydrocarbons resulting from depolymerization of biopolymers like cellulose linear chain polysaccharides $(C_6H_{10}O_5)_n$, hemicellulose comprising a diverse mixture of various polysaccharides categorised as xylans, mannans, mixed linkage β-glucans and xyloglucans, lignin which is a heterogenous amorphous biopolymer with an approximate formula of $(C_{31}H_{34}O_{11})_n$ and various extractives, which are the key constituents of biomass [211,215,217-219]. Biomass also contains ashes to some extent [220]. About 30-50% of the biomass contents by weight is cellulose, 10-40% by weight is hemicellulose, and 5-30% by weight could be lignin content based on the variation of the biomass types (i.e., softwood, hardwood, wheat straw, switchgrasses) (Table 5) [211]. Tannin (a naturally occurring water soluble phenolic compound) is another biopolymer that prevent the plant and algae from microbial, viral and microbial activities [221-223]. It has also been affirmed that the softness of the woods increases with the increased amount of lignin and extractives, whereas hardwood is comprised of more of the cellulose and hemicellulose biopolymers [220]. The overall activation energy requirement of the thermo-chemical breakdown of the biomass can be varied due to variation of quantity of these biopolymers. Kinetic modelling [224-226] of the individual thermal decomposition of cellulose [227-230], hemicellulose [231-233] and lignin [233-236] can explain the necessity of primary investigation of the feedstock compositions in order to optimise the desired product stream [237-239] among liquid, gaseous and char. Also, there could be combinations of a few parallel pathways to complete the pyrolysis of complex biopolymers like hemicellulose and lignin [205,224]. A higher heating rate of cellulose reduces char yield, whereas lowering the heating rate reduces the char yield from the thermos-degradation of lignin [224]. Lowering the heating rate also increases the activation energy requirement for thermos-degradation of both celluloses. Being multicomponent polymers, both hemicellulose and lignin respond to the heating rate based on their variations of components in the respective biomass [224]. A higher proportion of liquid from the biomass thermos-degradation is possible with higher amounts of cellulose and hemicellulose in the biomass feedstock [211]. Also, char yield reduces remarkably with the biomass feedstocks containing lesser amounts of lignin [240]. The pyrolysis process of the biomass produces water as a by-product [240]. Correlations for measuring higher heating values of the biomass feedstocks can be obtained from published articles [214,241] which have extensively analysed various correlations. Percentages of biopolymers in different biomass feedstocks and their heating values are presented in Table 5.

Although various research works have been performed on individual biopolymers (lignin, hemicellulose, and cellulose) of the biomass, it is found that the process is not economical in the industrial scale to separate these chemical compounds from the biomass feedstocks prior further reaction processes [239]. Besides, there are technical challenges to recover and distinctly separate the pure form of the hemicellulose and lignin. Shorter residence timing results in incomplete depolymerization of lignin. As a result, the lignin macromolecules are randomly broken to form liquid substances. But the longer residence periods can lead to secondary thermal cracking of the lignin macromolecules, which results in reduced liquid produced and adversely affects the bio-oil's quality [239]. Usually, the biomass pyrolysis process is a combination of thermal cracking of the key biopolymers in the biomass at various temperatures. Initially the moisture is removed from the biomass (<200°C), then the decomposition of lignin (280-500°C), cellulose (<240-350°C), and hemicellulose (200-280°C) take place in the fast pyrolysis process [205]. Most of the thermo-degradation process occurs within two-thirds of the maximum operating temperature of the pyrolysis process. Not only the rate of heating, reaction temperature, vapour residence time inside the reactor, and types of biomass feedstocks, but also the particle size of the feedstocks, gas sweeping rate, amount of moisture in the biomass, presence and catalyst types, reactor type and the variation of reactor types of the pyrolysis reaction process govern the yield characteristics [209,228,242]. Given that all other operating conditions are the same, the variation of particle size can significantly impact the yield quantification of char and liquid from the pyrolysis method. If the particle size is smaller, there is better opportunity to overcome the depolymerization obstacles of the complex hydrocarbons from biopolymers, thus increasing the rate of reaction to produce more of the desired product. On the other hand, the larger size of particles require more activation energy input to overcome the chain disintegration barriers,

Table 5

Energy value variation of biopolymers of various biomass feedstocks [211].

Biopolymers	Softwood(%)	Hardwood(%)	Wheat straw (%)	Switchgrasses(%)	Higher heating value(MJ/kg)	Activation Energy (KJ/mol)
Cellulose	35-40	45-50	33-40	30-50	16.16	227.27-287.56
Hemi-cellulose	25-30	20-25	20-25	10-40	16.10	30.09-194.35
Lignin	27-30	20-25	15-20	5-20	19.40	20-672.97

which can also lead to formation of more char due to secondary reactions [243]. If the particle sizes are small enough (i.e., fraction of mm scale), there will be better efficiency for rapid and consistent heat transfer to the particles to disintegrate and form desired yields [205]. In such cases, an efficient reactor bed is also necessary to help with conducting the reactions uniformly. Though the most frequently used reactor bed for pyrolysis process is the fluidised bed reactor, it struggles to meet that quick heat transfer requirement to complete the reactions of all the fed particles [205]. This matter was resolved with the use of ablative pyrolysis as well as auger pyrolysis methods to conduct the fast or flash pyrolysis [205,244,245].

Apart from the variation of sources of biomass feedstocks, studies on various pyrolysis processes and reactors are mainly available based on the yield [246-248], heating and temperature effect [249-252], particle size [253-256], vapour residence timing [257-259], and kinetic modelling [260-262]. Other key parameters considered for estimating the efficiency of the pyrolysis process are the moisture content and preheating for biomass drying, composition of biomass, feeding into the reactor, reaction period, reactor type, gas flow rate, types and quantity of catalysts, yield and char removal frequency, quenching or condensing efficiency of syngas, treating the non-condensing gases, and retreating or upgrading the bio-oil [263-265]. Typically, the bio-oil is a combination of water, insoluble lignin, aldehydes, ketones, organic acids, carbohydrates, phenol, furfurals and alcohols [257]. Optimal management of the pyrolysis process parameters can lead to an increased amount of desired chemical in the bio-oil. Selection of the appropriate type of pyrolysis reactor is imperative to obtain the desired yields from biomass feedstocks. The quantity of bio-oil yield differs with the type of pyrolysis reactor, e.g., ablative, bubbling fluidised bed and circulating fluidised bed reactors can yield about 75 wt.% bio-oil, compared with 70 wt.% by the spouted fluidised bed, 65 wt.% by the entrained flow reactor and rotating cone reactor, 60 wt.% by the vacuum pyrolysis reactor, about 45 wt.% by the rotating screw (auger) reactor and fixed bed reactor, as reported and reviewed in various publications [225,239,257,266-268]. Most commercial scale pyrolysis plants run on fluidised bed reactors. Typically, the pyrolysis plants can be categorised into 3 types based on the feeding methodology of the feedstock: (a) pneumatic (i.e., flow of atmospherically inert gases like Nitrogen, Argon, and flue gases); (b) mechanical (i.e., the way the materials are mixed or stirred to accomplish the desired thermal cracking); and (c) gravity fed [245,269]. A brief classification of the reactors is presented in Fig. 11 based on the discussions in publications [245,267].

Based on the technique for conducting the pyrolysis reactions and the desired yield types, the pyrolysis methods can be categorised as conventional (slow pyrolysis), flash, and fast [9,205]. Based on the yield requirements, flash pyrolysis can be divided into flash-liquid (for liquid), flash-gas (for syngas and various mixtures of chemicals) and ultra-fast pyrolysis [246,268]. Some more purpose driven pyrolysis processes are also in practice, namely, vacuum pyrolysis, carbonization, hydro-pyrolysis, and methano-pyrolysis [260,270-272]. Any of these types of pyrolysis reactions may occur in the absence or presence of catalysts [206,273-275]. Catalysts help with increasing the reaction rate by reducing the activation energies, optimise the liquid yield and reduce both gases as well as char yield from the feedstocks processed by the respective pyrolysis process [209,210]. Then the liquid substances can be reprocessed easily than the non-condensed gases [212,276].

Fast pyrolysis of biomass yields higher amounts of liquid (>75%) based on the dry feed quantity of biomass at optimal temperature, strictly maintaining a short vapour residence timing and effective cooling-condensation capacity of the biorefinery plant [217,276,277]. Initially, the fast pyrolysis process yields vapour of various hydrocarbons, non-condensable gases and char within few seconds [276]. The Waterloo flash pyrolysis process (WFPP) decomposes biomass materials into organic liquids without the presence of oxygen at continuous atmospheric pressure. Usually, it is a precisely regulated process that yields high amounts of liquid [205]. The process has been broadly exhibited using hardwood solid waste to yield as high as 70% organic liquid of the feed material [278].

Apart from fast pyrolysis, the methano-pyrolysis [279-281] and hydro-pyrolysis [271,272,282] processes have shown promising features on producing sustainable fuels more efficiently. The methano-pyrolysis process to crack the Methane gas or other hydrocarbons has the potential to establish technological linkage with the sustainable green fuel economy. The products of methano-pyrolysis are black carbon and hydrogen, carbon being a raw material for carbon-based industries and hydrogen being a fuel that would not produce any harmful

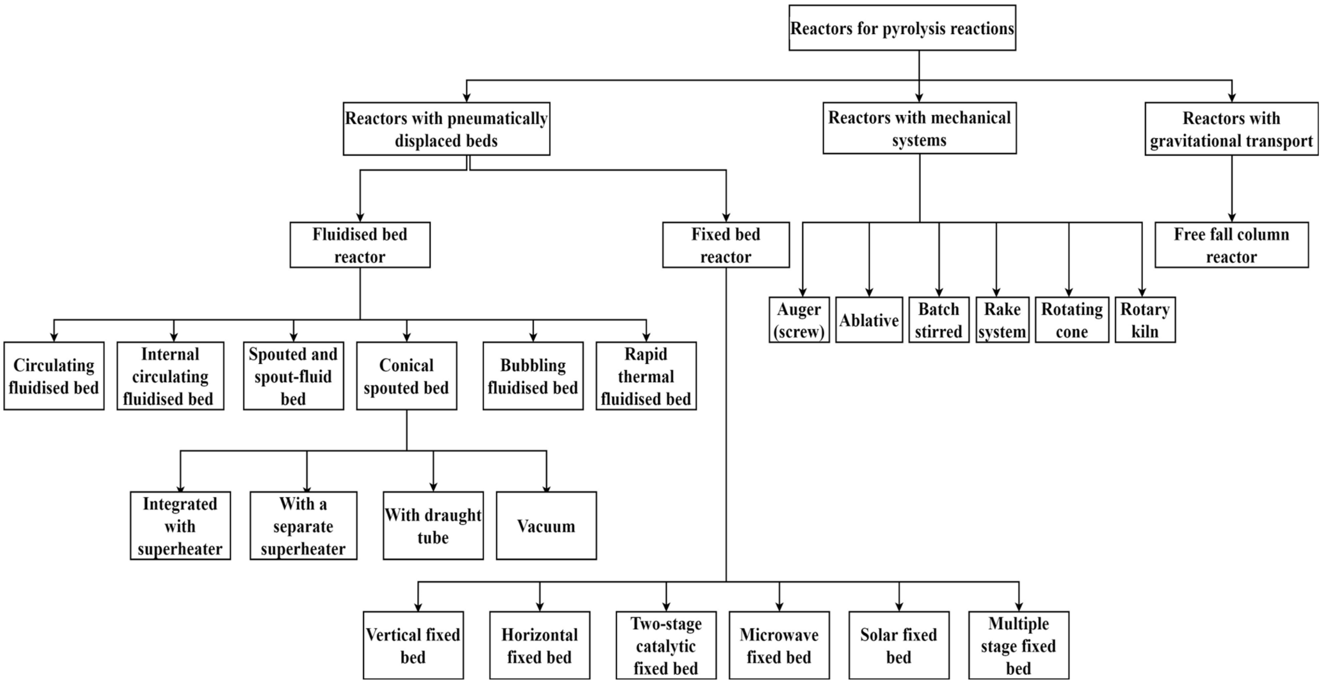


Fig. 11. Different types of reactors used for pyrolysis processes with or without catalysts [245,267].

emission products through combustion [283,284]. The Gibbs free energy values to conduct these chemical reactions are dependent on the reaction temperature [285]. The following process reactions [284] shown in Eqns. 24-28 will clarify the sustainability of methano-pyrolysis process.

$$\text{Natural gas combustion}: CH_4 + O_2(air) \rightarrow 2H_2O + CO_2 + 890kJ \tag{24}$$

$$\text{Hydrogen combustion}: 2H_2 + O_2(air) \rightarrow 2H_2O + 572kJ \tag{25}$$

$$\text{Carbon combustion}: C + O_2(air) \rightarrow CO_2 + 394kJ \tag{26}$$

$$\text{Steam methane reforming (SMR)}: CH_4 + 2H_2O + 206kJ \leftrightarrow CO_2 + 4H_2 \tag{27}$$

$$\text{Methano} - \text{pyrolysis of methane (natural gas)} : CH_4 + 74.52kJ \overset{819K}{\rightarrow} C(solid) + 2H_2 \tag{28}$$

Though combustion of 1 mole of natural gas produces 890kJ of heat energy, about 44.27% of the total heat is generated due to combustion of carbon. It can be observed that 1 mole of H_2 generates about 286kJ of heat due to its combustion. The steam methane reforming process needs 206 kJ of heat to produce 4 moles of H_2 along with 1 mole of CO_2. But the methano-pyrolysis process requires about 74.52kJ of heat energy (at 819k) to produce 2 moles of H_2 along with another industrial raw material, namely black carbon. Though there is more hydrogen production in the SMR process, production of CO_2 does not make the process completely sustainable. Conversely, methano-pyrolysis provides a sustainable way to convert hydrocarbon fuels into carbon free fuel for clean energy production, thus contributing to reduction of environmental pollution. Biomethane or other hydrocarbon gases obtained from the pyrolysis of biomass feedstocks can be processed in such a way so as to produce cleaner hydrogen fuel. But carbon removal and reactivity of carbon with the catalysts are key challenging factors for hydrocarbon cracking processes [286,287]. For a sustainable and economic way of hydrogen fuel production [269], it is necessary to compare these pyrolysis processes and reactors at optimal operating conditions on an industrial scale. The main challenge of biomass pyrolysis is the production cost and environmental concerns as identified by Jahirul et al [288]. The production of bio-oil using the pyrolysis process must overcome the economic, technical, and social barriers [288,289].

4.3.1. *Use of catalysts in the pyrolysis process*

Chemical looping of iron oxides has appeared as a favourable method to generate hydrogen with natural gas separation. Chen et al [290] in their research produced hydrogen from the pyrolysis of biomass using sol–gel-prepared $Fe_2O_3/MgAl_2O_4$ as an oxygen carrier. They found that the ideal gasification temperature is 950°C to attain a high conversion of optimum gasification temperature and gas yield through chemical looping. But the generated hydrogen was contaminated by CO_2 and CO severely due to the formation of coke during reduction. The hydrogen purity was increased by adjusting the atmosphere in the reduction area with the addition of steam and it was an efficient technique. The purity of hydrogen was achieved at 96% when the steam and oil ratio was 1.5 as compared to 84% when there was no steam. Addition of steam also enhances performance of the cycle by making the porosity more stable [291]. Table 6 presents different types of catalysts used for different types of reactors.

4.3.2. *Syngas to hydrogen production*

Hydrogen can be produced from syngas which is the by-product of some pyrolysis processes. Syngas can be produced from the pyrolysis of biomass which is available worldwide. This waste can be collected from municipal waste, industry waste and other sources. Biomass pyrolysis as explained in previous section can be utilised to produce hydrogen as well as syngas. The produced syngas can be used as feedstock to produce hydrogen. In addition to that, hydrogen can be produced directly using fast pyrolysis with a high temperature and a certain volatile phase residence time [204]. The process that is used to produce hydrogen is the reformer steam-iron process (combination of steam-iron process and conventional steam reforming process) which can be potentially employed to generate hydrogen in a decentralised facility for on demand hydrogen supply using syngas as the feedstock [292]. The beneficial features of the reformer-steam iron process are the use of two different reaction conditions, i.e., reduction process at atmospheric condition and the oxidation at higher pressure (~5 MPa) condition. In the case of syngas production from pyrolysis of biomass, the syngas can be directly processed by the iron-oxide (hematite, Fe_2O_3). Therefore, the pyrolysis of biomass and solid waste will help reduce the burden solid waste landfilling and the prosecution of hydrogen will add energy security.

4.3.3. *Biomass derived liquid bio-oil to hydrogen*

The highest product of the pyrolysis and thermochemical process of biomass is bio-oil. Different technique can be employed to produced hydrogen from the bio-oil. Bio-oil, an important biofuel, can be generated from thermochemical processes of biomass, such as hydrothermal liquefaction and pyrolysis [293-295]. Bio-oil is considered as a

Table 6
Various thermochemical processes of biomass [127].

Technology	Feeding	Reactor	Process Condition	Product yield
Fast pyrolysis	Lignocellulosic, wood waste	Circulating fluidised bed Reactor	Atm. pressure, 400–550°C, residence times of 1 s, particle sizes <0.5 mm	72% bio-oil, 12% gases and 16% char
Flash pyrolysis	Wood sawdust	Conical spouted bed reactor	425–525°C	bio-oil and gases
Slow pyrolysis	Algal biomass	TGA and Py-GC/MS	Low heating rate, 350–750°C, atm. pressure, long residence time	45–55% liquids, 25–35% gases, and 15–25 char
Air gasification	Pine sawdust	Fluidised bed reactor	700–900°C, ambient, Air with steam mixture	High temperature favoured H_2 and gas yields
Steam gasification	Olivine particles	Fluidised bed gasifier	770°C and a steam/biomass ratio of 1 with calcined dolomite	
Steam-oxygen gasification	woody biomass and agriculture residue	Circulating fluidised bed gasifier	800–820°C, steam to biomass ratios of 1.1–1.51; oxygen to biomass stoichiometric ratios (ER) of 0.36–0.4	20–25% H_2, 20–25% CO, 35–40% CO_2
Steam-air gasification	Wood waste	Fixed bed downdraft	Max. bed temp.: 900–1050°C and exit temp.: 700°C; equivalence ratios of 0.2–0.3	25–30% H_2, 40–45% CO, 20–25% CO_2
Steam-air gasification	Wood pellets	gasifier	Max. bed temp. of 950–1150°C and exit temp. of 150–400°C, and equivalence ratios of 0.24–0.35	25–35% H_2, 30–40% CO, 20–30% CO_2, 5–10% CH_4
Supercritical water gasification	lignin, cellulose and waste biomass	tubular batch reactor	Fixed heating rate of 30 °C/min to 650°C and residence time of 50s with K_2CO_3 and 20NiA 0.36 Ce/Al_2O_3 catalyst	30–40% H_2
Chemical looping gasification	biomass char	Fix-bed reactor	850°C with natural iron ore	H_2, CO
Solar gasification	pine and spruce wood	Tubular reactor with solar energy	1000–1400°C	35–45% H_2, High carbon conversion rate of 93.5%

favourable feedstock to substitute petroleum fuel for power generation because it has high energy density and bio-oil transport and storage is convenient as compared to gaseous fuel [296,297]. Bio-oil can be derived from various biomass feedstocks, green wastes (landfill wastes), animal wastes, and municipal wastes [184]. Reducing the capital and operational costs related to biomass feedstock production, logistics and process efficiency improvement can increase this industry's contribution effectively. The aqueous phase reforming (APR) can also be utilised to transform bio-derived liquid (bio-oil) or biomass into hydrogen directly like the autothermal reforming processes, partial oxidation, and steam reforming. Hydrogen is produced in the aqueous phase reforming process by decomposing the water-soluble organics elements at high pressure (~2 MPa) with relatively low temperatures (<300°C). The high pressure holds the elements in the liquid state and the low temperatures favours CO_2 production over CO, hence increase the hydrogen production without the water gas shift (WGS) reactor.

The process of reforming biomass-derived liquids and natural gas to produce hydrogen is same which includes the steps: The reaction of liquid fuel with steam at high temperatures in the presence of a catalyst which produces H_2, CO , and some CO_2. Additional H_2, and CO_2 are formed by reacting the CO with steam in the "water-gas shift" reaction. Lastly, the hydrogen is removed and then purified. The SRR and WGS reaction is presented in Eqns. 29-30.

$$\text{Steam reforming reaction (ethanol)} : C_2H_5OH + H_2O(+heat) \rightarrow 2CO + 4H_2 \tag{29}$$

$$\text{Water} - \text{gas shift reaction} : CO + H_2O \rightarrow CO_2 + H_2(+smallamountofheat) \tag{30}$$

4.3.4. Supercritical water reforming (SCWR)

The waste aqueous portion of the bio-oil produced from the thermal or thermo-catalytic processes may be converted into hydrogen gas or other hydrocarbons by the supercritical water reforming (SCWR) process, thus valorising the wastes. The aqueous portion may contain about 80% water as a result it may not be economical to recover the rest of the value-added products (e.g., acetic acids, hydroxy-acetones, 1-butanols, glucose [298]) from this waste stream. But the SCWR process can potentially convert the mixture into fuel or other usable chemicals at high pressure (up to 24 MPa), high temperatures (up to 800°C), and higher residence time (about 3-6 hours) to conduct the reaction process [298]. When the water portion of bio-oil is reformed by the SCWR process in a tubular fixed-bed reactor in the presence of Ni/Al_2O_3-SiO_2 catalyst, the method's yield of H_2 is 2.3 mol/mol at 800°C and 24 MPa [299].

Biomass pyrolysis can be used to produce hydrogen which will help alleviate the global waste management. The biomass can be collected from diverse sources which includes municipal solid waste, industrial waste in food processing, and agricultural waste in industry. These sectors are grappling to manage the huge waste they produced each day. This solid waste can be converted into hydrogen, solid char and syngas which can be synthesised later to convert into usable product. Different types of pyrolysis are available, selection of these process depends on the types of wastage, yield requirements and other factors. Appropriate pyrolysis process can be selected based on the method of feeding, types, and the process suitable for the pyrolysis of waste, economical consideration, and yield requirement. Purpose driven pyrolysis processes are also in practice, such as vacuum pyrolysis, carbonization, hydro-pyrolysis, and methano-pyrolysis, flash-liquid (for liquid), flash-gas (for syngas and various mixtures of chemicals). The pyrolysis process can crack not only the biomass but also the hydrocarbon, therefore this process can be used to crack the hydrocarbon for hydrogen production.

4.4. Biomass gasification

Another technique that can be used to produce the hydrogen from the biomass is the gasification process. In this process, biomass is converted into combustible gas mixture which has been used for decades for coal gasification. To produce hydrogen by the gasification process from biomass (e.g., Renewable organic materials, Agro-based crops or crop residues, forest residues, specific crops used only for energy production, organic municipal wastes, and animal wastes) requires a very high temperature (>700°C) non-combustion reaction in the presence of a controlled amount of oxygen. Hydrogen gas, CO and CO_2 are the typical products of the reaction. An adsorption or molecular membrane separation process can be used to remove hydrogen gas from this mixture. On the other hand, CO can react with waste to generate more hydrogen and CO_2 gases by a waste-gas shift reaction. Production of CO_2 is still a challenging task to handle in this process. A simplified example of the gasification and water gas shift reactions are presented in Eqns. 31-32.

Step 1: Gasification:

$$C_6H_{12}O_6(Glucose) + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + otherspecies \tag{31}$$

Step 2: Water-gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2(+smallamountofheat) \tag{32}$$

Integration of the pyrolysis process in the absence of oxygen with a water-gas shift reaction and catalytic hydrocarbon reforming can be an alternative to the usual high temperature gasification process. Various hydrocarbon gas mixtures are produced in the process of biomass pyrolysis. Then the mixture of hydrocarbons goes through catalytic hydrocarbon reforming to produce syngas mixture (i.e., hydrogen, CO, and CO_2). The water-gas shift reaction produces more hydrogen by the reaction between CO and steam, in which CO converts into CO_2 thus a significant amount of CO_2 is produced. Fig. 12 presents different kinds of gasifiers. Characteristics of different types of gasifiers are shown in Table 7. The table presents the operation parameter and the percentage of char conversion.

Syngas contains sulphur contaminants in the form of carbonyl sulphide (COS) and hydrogen sulphide (H_2S) which can be separated individually or collectively with other gases such as CO_2. Numerous processes which utilise physical or chemical adsorption or a combination are available to remove acid gas [300].

There are some technical and economic challenges with biomass in a decentralised H_2 production plant [302]. In a thermo-catalytic process like gasification, the plant will need a gasification reactor and portable purification unit (PPU) consisting of catalytic filter candles, pressure swing adsorbent (PSA) and a water gas shift reactor (WGS) in order to produce and separate H_2 gas from other gases [302]. Optimal adsorption time and linear velocity of the pressurised continuous feed of syngas through the adsorbent can lead to highly purified H_2 gas (99.99%) with more than two-thirds of the H_2 gas recovery from the gas mixtures [303,304]. In the presence of activated carbon and zeolite catalysts, the polybed PSA process integrated with the Skarstrom PSA cycle [305] or selective surface flow (SSF) membrane (thin nano-porous layer of carbon membrane supported on a macro-porous tube of alumina) [306] can improve the H_2 gas recovery from the waste gases, resulting in cumulative H_2 gas recovery of more than 90% [307,308]. The polybed PSA process can be comprised of 9 cyclic steps [309] (i.e., adsorption, concurrent depressurization I, concurrent depressurization II, concurrent depressurization III, counter-current depressurization, counter-current purge, counter-current pressurisation I, counter-current pressurisation II, counter-current pressurization III); or the Lofin process consisting of 9-cyclic steps [310] (i.e., adsorption, concurrent depressurization I, concurrent depressurization II, concurrent depressurization III, counter-current depressurization, counter-current purge, counter-current pressurization I, counter-current pressurization II, counter-current pressurization III) with the help of activated carbon (in the feed side) and zeolite (in the product separation side) catalysts [308].

Hydrogen can be produced from biomass using the biomass gasification process. Different types of gasification process are available, and each process has different operating conditions and efficiency. This

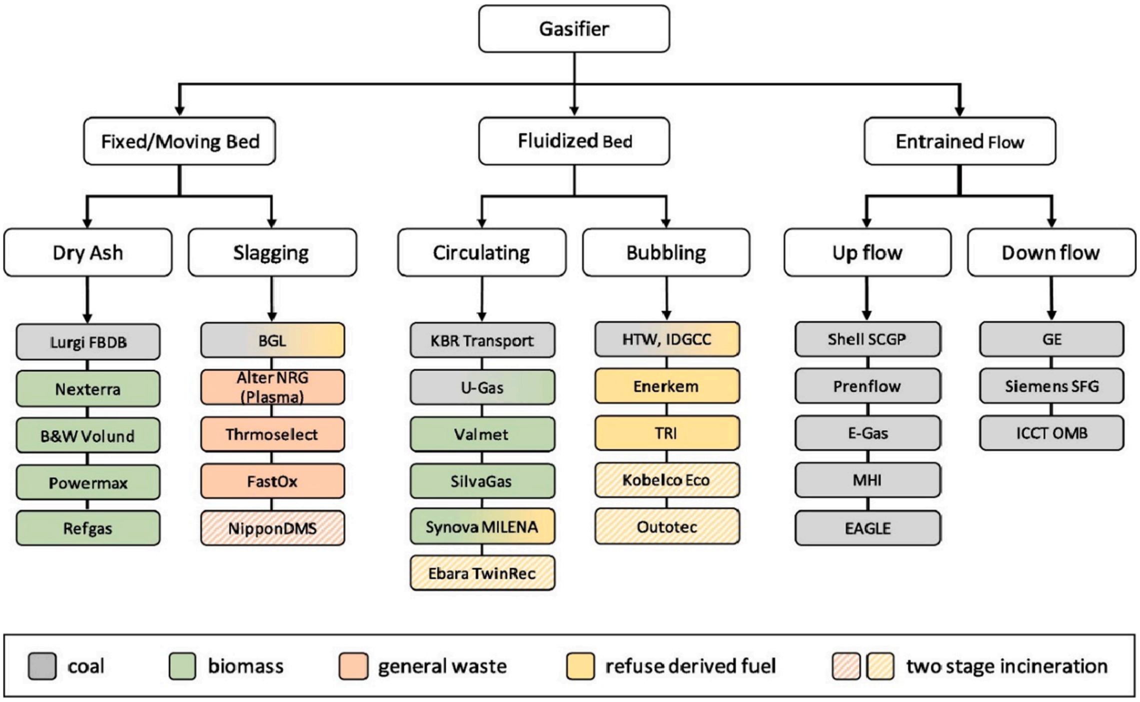


Fig. 12. Different types of gasifiers [300].

Table 7
Different types of gasifiers and their characteristic [301].

Gasifier types	Flows		Gasification temperature (°C)	Cold gas efficiency (%)	Char conversion (%)	Tar content (g/Nm^3)
	Biomass	GA				
Updraft	Downward	Upward	950–1150 exit temperature :150–400	20–60	40–85	1–150
Downdraft	Downward	Downward	900–1050 exit temperature :700	30–60	<85	0.015–1.5
Fluidised bed	Upward	Upward	800–900	<70	<70	10–40
Circulating fluidised bed	Upward	Upward	750–850	50–70	70–95	5–12
Entrained flow	Downward	Downward	1300–1500	30–90	60–90	≂ 0–0.2

process generates CO_2 which needs to be captured otherwise the process will have impact on the atmosphere and increase the carbon footprint. Synthetic e-fuel can be produced by capturing the CO_2 which will overcome the issue of producing CO_2. The process will benefit society by converting waste into useful fuel and alleviate global waste problem.

4.5. Decarbonisation

All the hydrogen production processes which use other than water as a feedstock produce carbon di-oxide. If the carbon di-oxide is released into the atmosphere, then the purposed of producing hydrogen will not serve. Therefore, to fulfill the objective of implementing new viable technologies for reduction of GHG emissions to the atmosphere due to combustion of fuels, the release of carbon compounds should be prevented. The possible options are direct decarbonisation, carbon capture and utilisation (CCU), and carbon capture and sequestration (CCS) [311]. The CCS method is encountering various economic, technological, and social challenges. Some specialists and researcher have concluded that "alternative emission mitigation technologies are potentially the only solution that could rescue us from the dire situation that we are heading toward by the end of this century" [312]. Therefore, the fossil-fuel Decarbonisation methods may create an crucial alternative in the technological portfolio that could alleviate the negative impact of climate change, facilitating the application of natural gas during a speedy energy shift [313]. There is a trade-off between the mitigation cost and the amount of Decarbonisation reached [99]. The most cost-effective techniques of Decarbonisation still use fossil feedstocks because of their low cost of removal and processing, but only provide average Decarbonisation quantities due to earlier underestimations of supply chain emissions contributions [99]. Solid carbon is safer, cheaper, and easier to store than that of gaseous CO_2. Furthermore, the pure carbon can be used in printing ink, car tyres, as well as in many new applications such as soil improvement and carbon electrodes [284]. Methane (CH_4, natural gas) contains the highest H/C ratio among all hydrocarbons. As a result, it is obvious to favour natural gas feedstock to produce hydrogen over other hydrocarbons. The cracking' or 'Decarbonisation' of 1 m^3 of methane will produce 2 m^3 of hydrogen. The decarburization process decomposes the hydrocarbons into carbon black and hydrogen gas with the help of either the "Hypro process" or "Hydrocarb process" [313,314]. Carbon can be used as raw material in various industries as activated carbon, carbon black and graphitic carbon [314]. The general reaction is presented in Eqn. (33) [313]:

$$CH_4 \xrightarrow{\Delta H^{\circ}=\frac{32.43}{kJ}kJ/mol^{H2}} C+2H_2 \tag{33}$$

The decomposition process is greatly governed by the input power, temperature, residence time, type and quantity of catalysts, feed rate and molar concentration of raw materials [313,315]. Though at 500°C only 10% of the feedstock is decomposed, about 95% feedstock can be decomposed at 1327°C [313,315,316]. Methane Decarbonisation can be a vital technology employed near the energy end-user on power-to-gas options [313]. The development of a sizable and modular method to separate methane into pure hydrogen and carbon may be relevant for domestic application of a few kW of energy, and for up to several MW for industrial uses. The schematic of methane Decarbonisation is presented in Fig. 13.

The incorporation of natural gas breakdown in the hydrogen economy and mobility is feasible based on the assessment with an IRR of 14%. Considering its incorporation in a combined cycle plant, even though the hydrogen generated is not expensive due to the higher scale, the efficiency of the plant declines to a 34% and is only offset by carbon taxes between 51 and 105 €/ton CO_2 [313]. Carbon and hydrogen production from cracking of hydrocarbon is shown in Fig. 14.

Hydrocarbons decomposition using single-step cracking (splitting, or dissociation, decomposition, pyrolysis, Decarbonisation, and dehydrogenation) facilitates the lowering of greenhouse gases by simultaneously producing important carbon products such as graphite or carbon black which can be used in carbon filaments or carbon nanotubes [317]. The catalytic method includes carbon and metal-based catalysts while plasma-based breakdown relies on thermal or non-thermal methods. Nearly all the recommended processes are appropriate to a range of liquid and gaseous hydrocarbon fuels, and a few of these methods can possibly generate a stream of high-purity hydrogen. There have been positive efforts to utilise catalysts to decrease the highest temperature of the thermal disintegration of hydrocarbons. Conventional catalysts employed are transition and noble metals such as Ni, Pd, Fe, Mo, Co, etc., which are deposited on the high surface area ceramic substrates such as SiO_2 and $A1_2O_3$, etc. Various publications reveal the application of carbon-based substances as catalysts for disintegration of hydrocarbons into H_2 and C. The non-catalytic disintegration methods are plasma jets, direct current generators, non-thermal low-temperature plasmas such as radio frequency, and microwave plasmatrons.

Burning fossil fuel or gaseous fuel produces cardon dioxide which has negative impact on the environment but burning hydrogen produces only water. Therefore, instead of burning fossil fuel or gaseous fuel, the fuels can be decomposed into carbon and hydrogen. Hydrogen can be used for energy and other industrial application and carbon can be used for printing ink, tyre manufacturing, carbon electrode and many other applications. The decomposition of hydrocarbon can be carried out with catalyst and without catalyst using plasma jet and plasmatron. The production of carbon di-oxide through this process can be captured and synthesised for synthetic fuel which can be used for engine fuel.

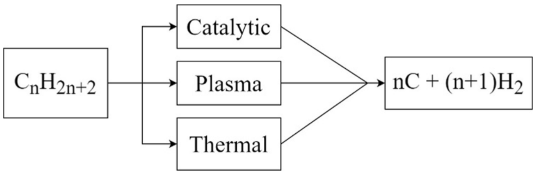


Fig. 14. Carbon production due to cracking of hydrocarbons in various methods [317].

4.6. Electrolysis

Electrolysis process can be used to produce hydrogen from water without any carbon di-oxide generation as a by-product. As this process does not release carbon di-oxide, this process is the greener hydrogen production process among all the process if the electricity used is generated from renewable sources. Electrolysis is a method of breaking water into oxygen and hydrogen by using a direct current, transforming electricity into chemical energy. At present, about 8 GW of electrolysis capacity are in operation globally [318]. Different kinds of electrolysers are characterised by the charge carrier and their electrolyte and can be categorised into: Solid Oxide (SO) electrolysers; Polymer Electrolyte Membrane (PEM) electrolysers; and Alkaline electrolysers. Similar to fuel cells, electrolysers comprise of an anode and a cathode which are separated by an electrolyte. Different electrolysers work in somewhat different ways, primarily due to the difference of electrolyte material.

The electrolyte in a polymer electrolyte membrane (PEM) electrolyser is a special plastic material. At the anode, water reacts to produce positively charged hydrogen ions (protons) and oxygen. The electrons travel through an outside circuit and the hydrogen ions particularly travel through the PEM to the cathode. Hydrogen ions join with electrons at the cathode from the exterior circuit to produce hydrogen gas as shown in Eqns. 34-35.

$$\text{Anode Reaction}: \ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{34}$$

$$\text{Cathode Reaction}: \ 4H^+ + 4e^- \rightarrow 2H_2 \tag{35}$$

Alkaline electrolysers work by carrying hydroxide ions (OH^-) from the cathode to the anode through the electrolyte with hydrogen being produced on the cathode side. Electrolytes of liquid alkaline solution of sodium or potassium hydroxide have been commercially available for

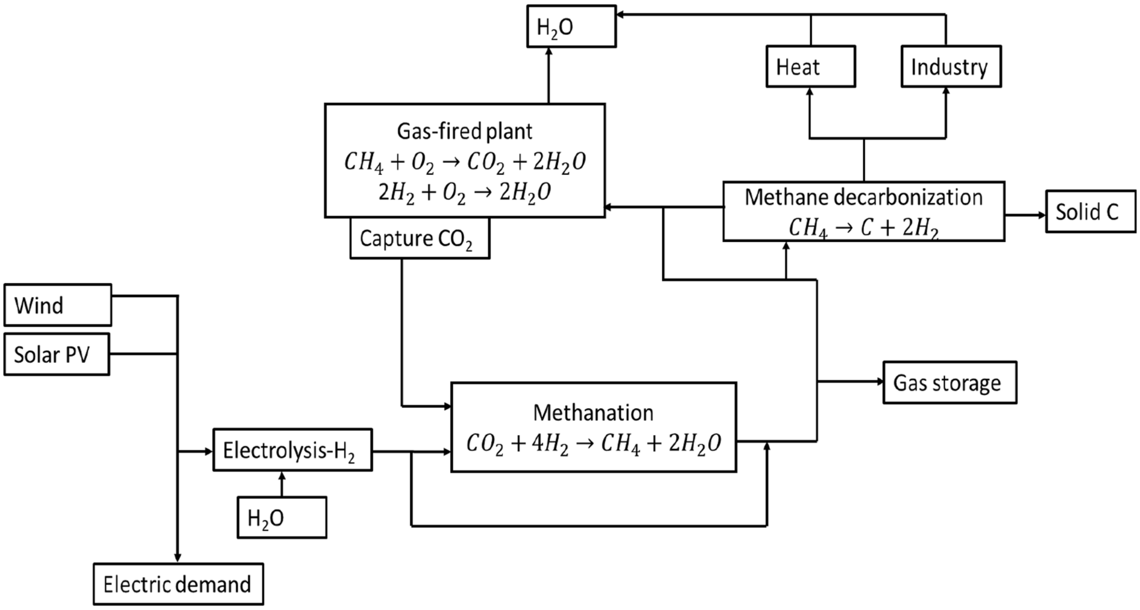


Fig. 13. Methane Decarbonisation near the end–user in power-to-gas options, redrawn from ref [313].

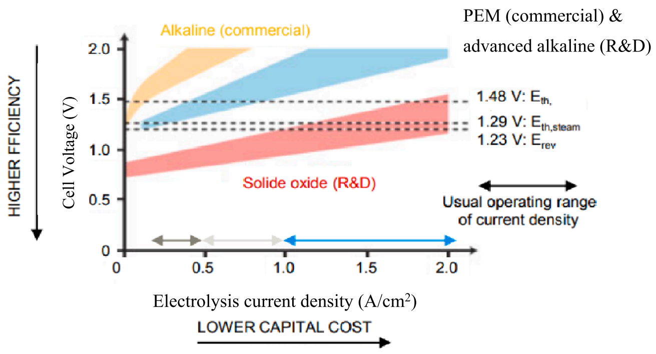


Fig. 15. Performance of different electrolysers [319].

many years for electrolysers. Newer attempts of utilising solid alkaline exchange membranes as the electrolyte are showing potential at the laboratory size.

SO electrolysers, which utilise a solid ceramic electrolyte that selectively carries negatively charged oxygen ions (O^{2-}) at high temperatures, produce hydrogen in a somewhat unique way. Water at the cathode unites with electrons from the exterior circuit to produce hydrogen gas and negatively charged oxygen ions. The oxygen ions go through the solid ceramic membrane and react at the anode to produce oxygen gas and produce electrons for the external circuit. Solid oxide electrolysers must work at high temperatures sufficient for the solid oxide membranes to operate properly (about 700°–800°C, PEM electrolysers, 70°–90°C, and commercial alkaline electrolysers, 100°–150°C). The SO electrolysers can efficiently utilise the heat available at these high temperatures (from different sources, like nuclear energy) to reduce the total of electrical energy required to generate hydrogen from water. The performance of various types of electrolysers are presented in Fig. 15. The figure shows that the solid oxide (SO) has the highest efficiency, but this electrolysis is in the R&D state.

Though alkaline electrolysers at present have higher efficiencies than electrolysers using PEM and solid electrolytes but SO electrolysers have considerably higher possibility for potential cost reduction and efficiency improvements (Fig. 15). Different hydrogen production processes and their key data are presented in Table 8.

The specifications of alkaline, PEM and SOE production processes are presented in Table 9.

Cracking the water into hydrogen and oxygen is greener hydrogen production process than any other process provided that the electricity used for electrolysis is generated renewably. This process does not produce any harmful gasses as by product nor does the combustion of hydrogen. The main electrolysis process used for the decomposition of water into hydrogen and oxygen are alkaline, PEM and SO. Both PEM and SO are in initial stage and need further research and development for their performance improvement. J corridor et al [322] presented the comparative performance of different hydrogen production method such as heterogeneous photocatalytic (HETPHP), homogeneous photocatalytic (HOMPHP), and hybrid photocatalytic (HYBPHP) using photocatalytic hydrogen generation technique. They found that HETPHPs can be used for large-scale application and this method offers longer operation times due to the high semiconductor photocatalyst stability and ability to be recovered from the treated solution. They concluded that highest H_2 production rates been achieved with HOMPHPs or HYBPHPs using visible light irradiation.

5. Hydrogen storage, transmission, and distribution

Many methods are available to produce hydrogen efficiently although there are pros and cons of each of these techniques. The main draws back of the hydrogen economy is the storage, transmission, and

Table 9
Typical specifications of production processes [321].

Specification	Alkaline	PEM	SOE
Technology maturity	State of the art	Demonstration	R &D
Cell temperature °C	60–80	50–80	900–100
Cell pressure, kPa	<3000	<3000	<3000
Current density, A/cm^2	0.2–0.4	0.6–2.0	0.3–1.0
Cell voltage, V	1.8–2.4	1.8–2.2	0.95–1.3
Power density, W/cm^2	Up to 1.0	Up to 4.4	-
Voltage efficiency, %	62–82	67–82	81–86
Specific system energy consumption, kWh/Nm^2	4.5–7.0	4.5–7.5	2.5–3.5
Partial load range, %	20–40	0–10	-
Cell area, m^2	<4	<300	-
Hydrogen production, Nm^2/hr	<760	<30	-
Stack lifetime, hrs.	<90000	<20000	<40000
System lifetime, yrs.	20–30	10–20	-
Hydrogen purity, %	>99.8	99.999	-
Cold start-up time, min	15	<15	>60

Table 8
Different types of hydrogen production processes and their key data [320].

Technology	SMR	POX	Electrolysis	Gasification
Energy input	NG+ electricity	HC+ electricity	Electricity	HC+ electricity
Efficiency %	70–85	60–78	62–82	50–70
Size (Nm^3/h)	10000–20000	10000–20000	0.5–10	10000–20000
Lifetime	2–5 years	2–5 years	40000 hrs.	2–5 years
Market share (%) (2012)	48%	30%	4%	18%
Production (2011) cost (€/Nm^{3}H$_2$)	0.05–0.1	0.07–0.15	0.16–0.30	0.05–0.1
Cost breakdown (%)	30% materials 40% process 30% labour	30% materials 40% process 30% labour	50% materials 30% process 20% labour	30% materials 40% process 30% labour
Projection				
Efficiency %	70–85 (2015) 70–85 (2020) 75–85 (2030)	60–78 (2015) 60–80 (2020) 65–80(2030)	50–80 (2015) 55–80 (2020) 80–85(2030)	50–70 (2015) 55–70 (2020) 60–75(2030)
Production cost (€/Nm^{3}H$_2$)	0.090 (2015) 0.085 (2020) 0.080 (2030)	0.110 (2015) 0.105 (2020) 0.100 (2030)	0.15–0.27 (2015) 0.13–0.20 (2020) 0.10–0.15 (2030)	0.095 (2015) 0.090 (2020) 0.085 (2030)
Lifetime	2–5 years (2015) 2–5 years (2020) 2–5 years (2030)	2–5 years (2015) 2–5 years (2020) 2–5 years (2030)	40000 h (2015) 45000 h (2020) 65000 h (2030)	2–5 years (2015) 2–5 years (2020) 2–5 years (2030)
Market share	48% (2015) 45% (2020) 40% (2030)	30% (2015) 25% (2020) 20% (2030)	5% (2015) 15% (2020) 30% (2030)	17% (2015) 15% (2020) 10% (2030)

distribution. More research should focus in this area to overcome these drawbacks. A major hurdle in the hydrogen economy lies in its transport and storage. Being an ultralight gaseous molecule, the density of hydrogen at the normal atmospheric condition (20°C and 100 kPa pressure) is 0.082 kg/m^3 and its lower heating value (LHV) is 119.22 MJ/kg [323]. Hydrogen has a very low liquid state temperature range profile. It turns into liquid below -253°C and is solid below -259 °C, thus the boiling point of hydrogen is just greater than >-253°C [77]. Unless cryogenic compression is adopted [324], its boiling point can be increased up to -240°C by applying a maximum of 1.4 MPa pressure [77]. The cost of distribution from the hydrogen generating facility to the consumers may require about 40-75% of the total hydrogen supply chain expenses [325]. On-board tanks are a major limitation of using hydrogen as an automobile fuel because of low energy density [85]. Characteristics of different technologies of hydrogen conversion and storage are shown in Table 10.

The carbon footprint of different pathways to hydrogen is presented in Fig. 16. The figure shows that the lowest carbon footprint is from centralised electrolysis and the highest is decentralised electrolysis. The figure also shows that the highest carbon footprint comes from transformation near market.

5.1. Liquefaction of hydrogen

Hydrogen can be compressed into liquid hydrogen at high pressure and low temperature. This process requires high energy compared to other storage technique. For a variety of reasons, the most favourable option to store hydrogen is as liquid hydrogen (LH_2)[81]. Different methods are used to produce liquid hydrogen [81], but these are mainly categorised as central production and distributed production facilities. The hydrogen liquefaction process consumes a huge amount of energy; as a result, the reduction of energy consumption in this process as well as increasing the efficiency will reduce the cost of the entire process [327]. The precooled liquefaction method and cascade liquefaction method are the two parts of hydrogen liquefaction methods based on the refrigeration cycles.

The boiling point of hydrogen is –253°C so it is estimated that the liquefaction of hydrogen requires 40% of the LHV of hydrogen [77]. It could be economical to convert the hydrogen into a liquid substance if the liquified hydrogen is directly used in the respective applications. At a temperature of –30°C , carbon steel turns brittle and is susceptible to fracture [77]. At the boiling temperature of hydrogen, air in contact with the hydrogen line may liquify which can create a fire hazard. Moreover, hydrogen cannot be kept in liquid form for an indefinite period. Present automotive hydrogen storage tank technology gives a venting (or "boil-off") rate of around 1 to 2% per day due to embrittlement of the tank material to this gas. A schematic of hydrogen liquefaction is presented in Fig. 17.

Capital costs for processing the liquid hydrogen (LH_2) has been a critical concern due to higher real energy demand (kWh energy input per kg of LH_2). But if the energy demand drops below 6 kWh per kg of LH_2, then the liquefaction process could be an economic one [329]. Numerous alternatives have been examined to solve the low-density problem of hydrogen like transporting of hydrogen in the liquid state rather than the gaseous state. Liquid hydrogen has a higher energy density than that of gaseous hydrogen and is lower than that of the conventional fossil fuels when being transported long distances (Fig. 18). The boiling point of hydrogen is -253°C which is very low; as a result, 30-40% of the energy of the hydrogen is needed to liquefy it and additional energy is needed to keep the hydrogen in liquid state during storing and transporting to reduce the losses. The energy densities of different fuels are presented in Fig. 18.

5.2. Hydrogen carriers

Apart from liquefaction of hydrogen, hydrogen can be combined with other chemical or element which is called hydrogen carrier and can be transported. Then the hydrogen can be released from the carrier using different technique and use to serve the purposes. The primary candidates for the role of hydrogen carriers are liquid ammonia, organic molecules (e.g., methanol), liquid organic hydrogen carriers (LOHCs), and metal alloy hydrides. All the candidates contain carbon except ammonia and metal alloy hydrides. Dibenzyl toluene, which is safe to use and currently used as heat transfer fluid, can be used as alternatives to LOHC. However, the production and handling in large quantities is limited except in specified chemical facilities, although it does not pose a safety issue with strict controls in place. Ammonia can be used as a hydrogen carrier and can also be cracked into hydrogen as shown in Fig. 19. The advantage of using ammonia as a hydrogen carrier are:

- Ammonia is 6 times more compact than hydrogen stored at 20 MPa.
- Ammonia requires low pressure storage and transportation.
- Ammonia is free from carbon and high-density storage of H_2.
- Ammonia can reduce the cost of storage and transportation.

The hydrogen carrier must be generated using a renewable source which should not have any carbon footprint for the carrier then it can be called zero-carbon or very low-carbon, otherwise the overall process

Table 10

Characteristics of different technologies of hydrogen conversion and storage [326].

Application	Capacity	Efficiency	Initial investment cost	Lifetime	Maturity
Alkaline FC	Up to 250 kW	~50%(HHV)	USD 200-700/kW	5000-8000 hr.	Early market
PEMFC stationary	0.5-400kW	32%-49% (HHV)	USD 3000-4000/kW	~60000 hr.	Early market
PEMFC mobile	80-100 kW	Up to 60% (HHV)	USD -500/kW	<5000 hr.	Early market
SOFC	Up to 200 kW	50%-70% (HHV)	USD 3000-4000/kW	Up to 90000 hr.	Demonstration
PAFC	Up to 11 MW	30%-40% (HHV)	USD 4000-5000/kW	30000-60000 hr.	Mature
MCFC	kW to several MW	More than 60% (HHV)	USD 4000-6000/kW	20000-30000 hr.	Early market
Compressor 18MPa	-	88%-95%	USD -70/kWH_2	20 years	Mature
Compressor 70MPa	-	80%-91%	USD 200-400/kWH_2	20 years	Early market
Liquefier	15-80 MW	~70%	USD 900-2000/kW	30 years	Mature
FCEV on-board storge tank 70 MPa	5 to 6 kg H_2	Almost 100% without compression	USD 33-17/kWh (10000 and 500000 units produced/year	15 years	Early market
Pressurised tank	0.1-10 MWh	Almost 100% without compression	USD 6000-10000/MWh	20 years	Mature
Liquid storage	0.1-100 GWh	Boil-off steam: 0.3% loss per day	USD 8000-10000/MWh	20 years	Mature
Pipeline	-	95% inc. compression	Rural: USD 0.3-1.2 M /km, Urban: USD 0.7-1.5 M/km (Depend on diameter)	40 years	Mature

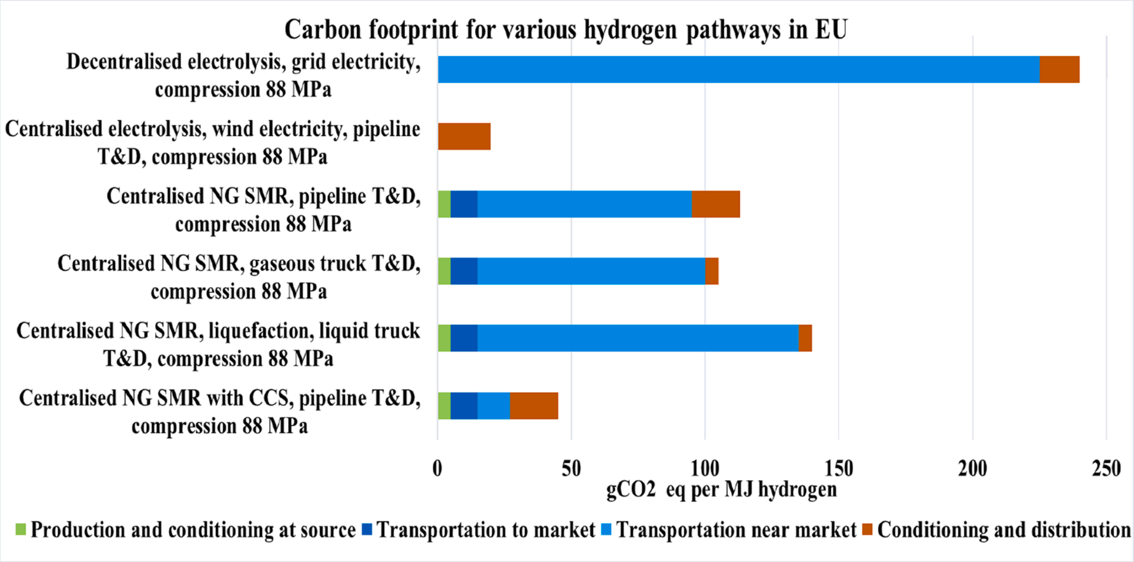
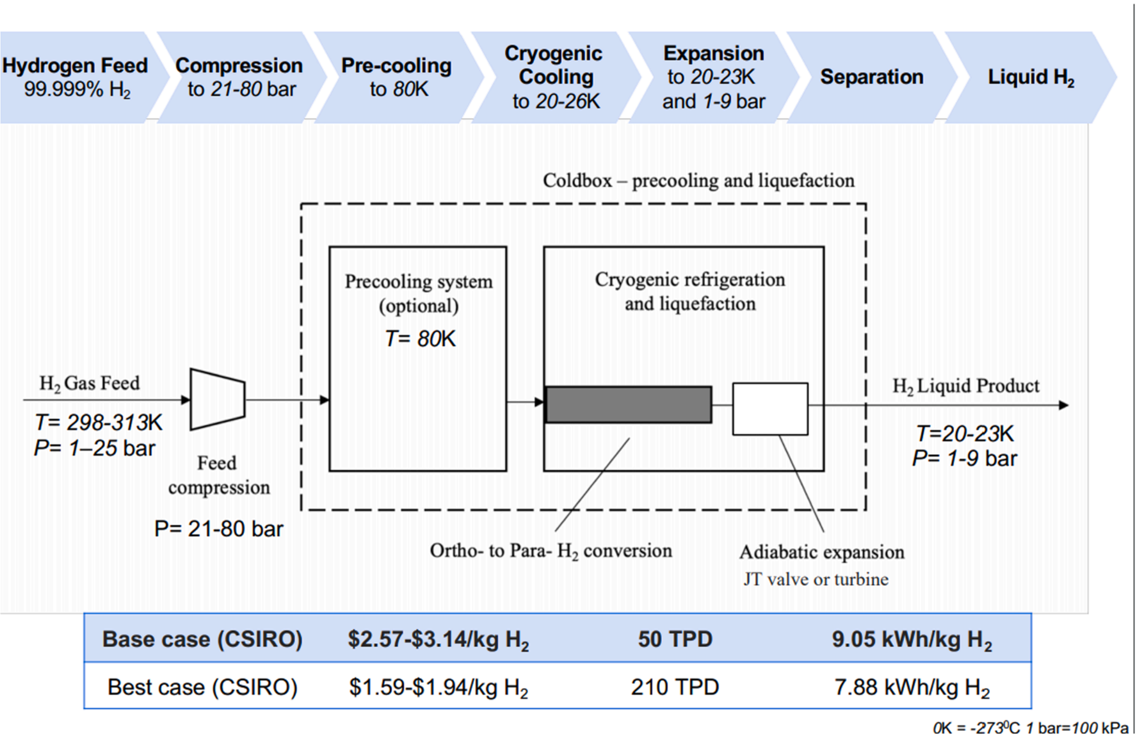


Fig. 16. Carbon footprint of different hydrogen pathways, redrawn from ref [336 .



Base case (CSIRO)	**\$2.57-\$3.14/kg H_2**	**50 TPD**	**9.05 kWh/kg H_2**
Best case (CSIRO)	\$1.59-\$1.94/kg H_2	210 TPD	7.88 kWh/kg H_2

Fig. 17. Hydrogen liquefaction process schematic [328].

cannot be called net-zero. The cost of transporting hydrogen in the liquid form is considerably lower than that of the compressed gas form as obtained from the feasibility study [332]. The cost of transporting gaseous hydrogen is £51.85/MWh per 100 miles (£1.73/kg H_2) and the cost of transporting the equivalent liquid ammonia is £6.55/MWh (£0.22/kg H_2) as of 2018; these are operator costs published by the Freight Transport Association [333]. Lamb et al. [334] reviewed the ammonia as hydrogen carrier and discuss the decomposition, separation, and purification of hydrogen. They found that dense-metal membranes are uninhibited by ammonia and can achieve the required product purity but recommended further research for efficiency improvement and cost reduction. Firman et al. [335] reviewed different ammonia production process such as thermochemical and electrochemical processes. They pointed out that the thermocyclic process of metal oxide by splitting the NH_3 synthesis reaction into two reactions is the promising method for NH_3. They also found that the electrochemical can integrate renewable energy. This process can operate at high and low temperature, but high temperature yields more NH_3 than low temperature process.

The remnant of ammonia in the fuel supply during the cracking of ammonia into hydrogen can poison the PEM fuel cell. The palladium catalyst based purifying technology of hydrogen is very expensive which needs processing at 600°C and 1 MPa, thus the process has not been economically feasible to date.

The metal oxide method can operate at below 300°C and 100 kPa, thus reducing the system cost. RenCat technology utilises a cheap mixed

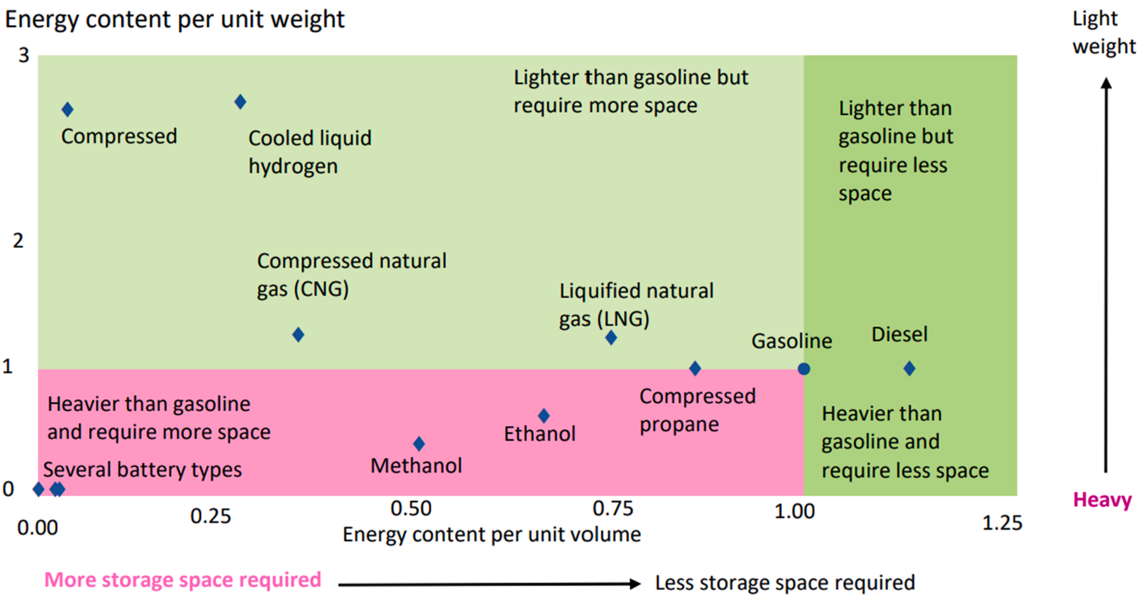


Fig. 18. Comparison of energy densities of conventional fuels, redrawn from ref [330,331].

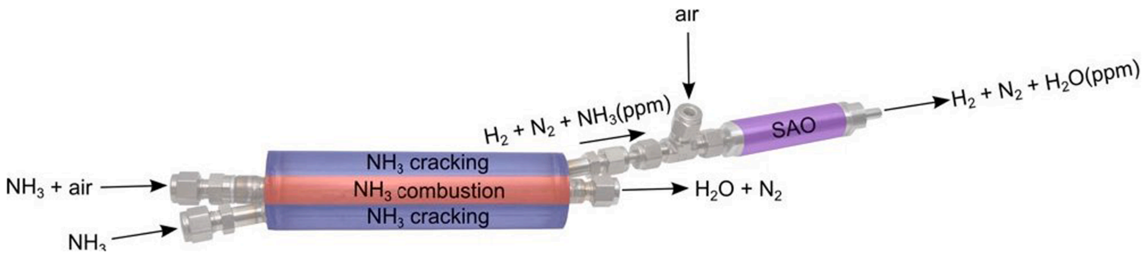


Fig. 19. Schematic process of cracking ammonia into hydrogen.

Table 11
Comparison among hydrogen storage systems [337].

Fuel / Storage System	Pressure (kPa)	Energy Density (GJ/m^3)	Specific Volumetric cost (US$/m^3)	Specific Energy Cost (US$/GJ)
Ammonia gas / pressurised tank	1000	13.6	181	13.3
Hydrogen / metal hydride	1400	3.6	125	35.2
Gasoline (C_8H_{18}) / liquid tank	100	34.4	1000	29.1
LPG (C_3H_8) / pressurised tank	1400	19.0	542	28.5
CNG (CH_4) / integrated storage system	25000	10.4	400	38.3
Methanol (CH_3OH) / liquid tank	100	11.4	693	60.9

metal oxide-based catalyst to oxidise the remnant of ammonia after cracking to produce a PEMFC quality H_2. The catalyst, which is pending patent, oxidises only ammonia in the H_2 stream and thus makes ammonia concentration zero which is called selective ammonia oxidation (SAO)[336]. The schematic of cracking ammonia into hydrogen is shown in Fig. 19. The differences of various hydrogen storage systems are presented in Table 11.

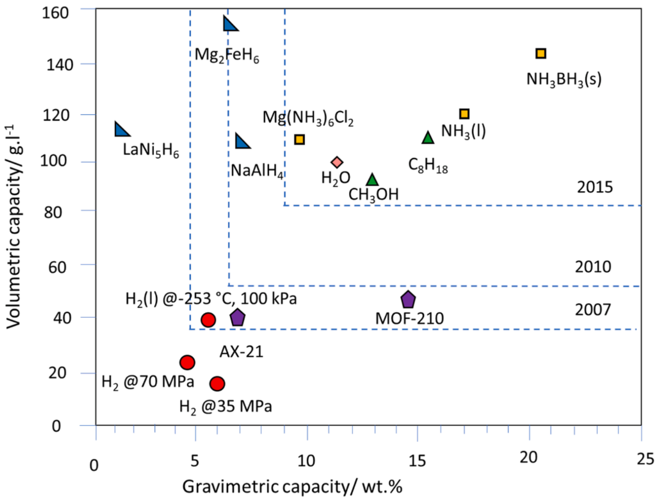


Fig. 20. Volumetric capacity of different carriers [337].

The volumetric capacities of different hydrogen carriers are presented in Fig. 20. The figure shows that the Mg_2FeH_6 has the highest volumetric capacity and hydrogen at 35 MPa has the lowset volumetric capacity. From the figure it can be concluded that the hydrogen combined with carrier has better volumetric capacity than that of hydrogen alone.

Ammonia Borane (NH_3BH_3) can be used as a hydrogen carrier. Its thermal decomposition process and the chemical equations are

Table 12
Ammonia borane decomposition of hydrogen [175].

Thermal Decomposition	Chemical Equation	Processes
First step (110 °C)	$NH_3BH_3 \rightarrow NH_2BH_2 + H_2$	The first yield of hydrogen
Second step (125 °C)	$nNH_2BH_2 \rightarrow (NH_2BH_2)_n$	Intramolecular polymerisation
Third step (150 °C)	$(NH_2BH_2)_n \rightarrow (NHBH)_n + nH$	The second yield of hydrogen
Remaining step (500 °C)	$(NHBH)_n \rightarrow nBN + nH_2$	generation of excess hydrogen

presented in Table 12.

Ammonia has a lower storage cost over 182 days of 0.54 \$/kg-H_2 in contrast to hydrogen at 14.95 \$/kg-H_2. In addition to that, the volumetric energy density of ammonia is high at 7.1–2.9 MJ/L, and ammonia is easy to produce, handle and distribute. Ammonia has better commercial viability than that of pure hydrogen. If ammonia is produced using renewable sources, it will add more advantages [338-340].

The properties and advantages of ammonia are:

- Free from carbon and greenhouse gas.
- The energy density of ammonia is 22.5 MJ/kg whereas that of coal is 20 MJ/kg.
- At normal temperature and 0.8 MPa, ammonia can be compressed to liquid.
- Existing infrastructure can be used for ammonia storage and distribution.

The ammonia decomposition process is schematically shown in Fig. 21.

The comparison of hydrogen density is presented in Table 13. As ammonia has more energy than hydrogen, an ammonia tank (1 MPa) with a similar volume of hydrogen holds 2.5 times the energy of a hydrogen tank (70 MPa), so a hydrogen tank of 770 L (350 kg) can be substituted by 315 L of ammonia (172 kg) [342].

5.3. CO_2 capture and storage (CCS), utilization (CCU)

Carbon di-oxide produced from the pyrolysis and other processes must be stopped from releasing into the atmosphere. This can be done by capturing the carbon di-oxide and storing carbon di-oxide or capturing the carbon di-oxide and using caron di-oxide to produce usable chemicals. Therefore, to claim the processes to produce renewable or cleaner fuels, the reaction by-products such as CO and CO_2 must be captured and sequestrated from atmosphere. The concentration of CO_2 in the exhaust gas is high, so steam methane reforming (SMR) methods are potential candidates for the usage of carbon capture and sequestration (CCS) technology which can decrease 80% of carbon emissions [343]. Various options are available to generate low-carbon hydrogen and each method has a different decarbonisation process and the methods have several obstacles of production, cost and the scale of production [344]. The GHG emissions in terms of CO_2 equivalent have been found to be varying due to variations of processes and feedstocks [216]. CCS technologies can be divided into biological, non-biological and engineering approaches [345]. The non-biological process can be categorised as oceanic [346-348], geological [349,350] and chemical sequestration [351]. The biological process [352] can be oceanic fertilization [353] and terrestrial sequestration [354], whereas the latter can be categorised as soil-carbon sequestration and Phyto-sequestration processes. Table 14 presents a brief comparison of various CCS processes.

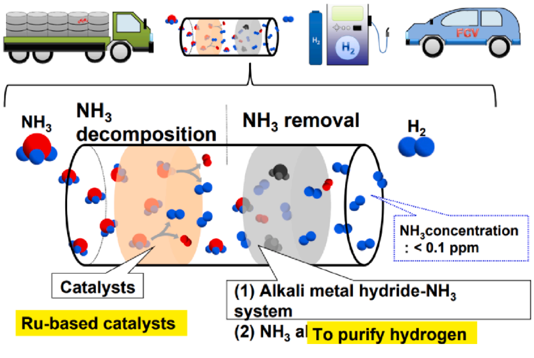


Fig. 21. Schematic presentation of NH_3 decomposition [341].

Table 13
Volumetric hydrogen density of liquid NH_3 and H_2.

Pressure, temperature		H_2 density of NH_3/ H_2 density of H_2
Liquid H_2	Liquid NH_3	
0.1 MPa, -253°C	1 MPa, 25°C	1.5 times
0.1 MPa, -253°C	0.1 MPa, -33°C	1.7 times
1 MPa, -242°C	1 MPa, -25°C	2.2 times

Table 14
Brief contrast of various CCS processes [345].

Methods of CCS For all the CCS methods	Advantages Potential reduction of GHG.	Limitations Storage longevity and sustainability issue.
1. Nonbiological		
i. Oceanic (Direct Injection)	Less leakage. Larger sinks for CO_2.	Limited efficiency due to injection depth requirement. Adversity to marine biota.
ii. Geological	Greater sink depth favours CCS stability. Enhanced oil and natural gas recovery. Tertiary sequestration.	Not fully durable to leak free storage. Expensive. Unpredicted storage volume.
iii. Chemical	Longer CO_2 storage period and lower leakage. Thermodynamically more favourable.	Unsuitable for industrial applications. Higher temperature required to overcome slow reaction rates.
2. Biological		
i. Oceanic (ocean fertilization)	Fixing CO_2 issues of Phytoplankton.	It can deteriorate the ecology of the oceanic system.
ii. Terrestrial		
a) Soil carbon sequestration	The naturally occurring CO_2 sequestration can be further modified with efficient ecosystem establishment.	Various factors relating to the environment limit the effectiveness of the process.
b) Phyto-sequestration	Larger sinks for CO_2. Economic. The natural photosynthesis can help in CCS.	Deforestation risk is emerged. Both the global scale plantation and photosynthesis efficiency need to be increased.
3. Engineering	With proper management to improve the naturally occurring photosynthetic process, it can lead to efficient CCS. For instance, engineering microbial CCS technology has potential to become great carbon sink [355].	Expensive and still more R&D works need to be done to make the process successful. For instance, the engineering microbial CCS process still require lot of R&D to achieve target efficiency [355] .

Moreover, Nanda et al. [356] and Al Mamoori et al. [357] reviewed various CCS technologies and categorised them under three key routes, i.e., biological (algae and bacteria, dedicated energy crops, and coalbed methanogenesis), physiochemical (absorption, adsorption, methane separation, membrane separation and cryogenic distillation), and geological routes (oceanic storage and biochar). In such classifications, the physiochemical processes are mainly considered as fast-track technologies. Biological processes have been recognised as sustainable approaches for carbon fixation, but the geological routes may require dealing with carbon trading to establish larger industrial applications [356]. Regardless of the CCS technologies, the main stages of CO_2 capture are at pre-combustion (about 15-40% v/v CO_2 can be captured), post-combustion (about 4-14% v/v CO_2 can be captured) and oxy-fuel combustion (about 80% v/v CO_2 can be captured) [356]. All of these options and processes have their individual challenges and advantages, but mostly include the increasing expenditure due to higher capital cost, scalability, energy penalty, integrating and coordinating the auxiliary process plants, air capture technology implementation and analysis of the combustion stream yields [351,356,358].

Typically, CO_2 sequestration requires various steps involving the capture, pressurization, carrying, and pumping of liquid CO_2 (L-CO_2) below the ocean or into geologic developments. At normal temperature and pressures in the ocean, CO_2 will remain as a gaseous form at less than 500 m depth and in the liquid form at more than 500 m depth. The L-CO_2 will float in ocean water at a depth down to 3000 m and will sink below that depth because L-CO_2 has relatively low density (Fig. 22).

The CO_2 Lake idea shown in Fig. 22 may require further innovative technology and higher expense, but the lake can possibly reduce the seepage to the atmosphere and exposure to biology. The economics of CO_2 sequestration related to hydrogen generation from fossil fuels are reported in the literature [348,359,360]. Some challenges [344] are still there for CO_2 sequestration: (i) reduction of cost; and (ii) Technical knowledge of the artificial lake (e.g., volume, longevity, and, most importantly, ecological impact). The crucial risk issues are vague prolonged environmental effects, catastrophic release of CO_2 from the underwater sink due to oversaturation, and the substantially reduced pH value of sea water surrounding CO_2 disposal under the sea. More R&D advancement is required to resolve these issues. Environmentally "benign" sequestration (EBS) of CO_2 [344,361], mineral carbonation [362], enhanced oil recovery (EOR) [361] and mixing liquid-carbon dioxide [363,364] with pulverised limestone and water to produce aqueous Ca^{2+} and HCO_3^- (Eqn. (36)) will all lessen the environmental effects (e.g., pH change) of dumping CO_2 into the ocean as well as enhance the average specific gravity of the system to 1.4g/ml, thus enabling CO_2 disposal at ocean depths higher than 1000 m.

$$CO_2(l) + CaCO_3(s) + H_2O(l) \leftrightarrow Ca^{2+}(aq) + 2HCO_3^-(aq) \tag{36}$$

It has been projected that there may be about 850 CCS projects around the world by 2030, and about 3,400 by 2050 (Fig. 23) in order to capture the targeted amount (about 10 Gt) of CO_2 from various energy sectors [358]. As a result, it has been projected that it may require about 5070 billion USD of cumulative investment between the period of 2010 and 2050 [358].

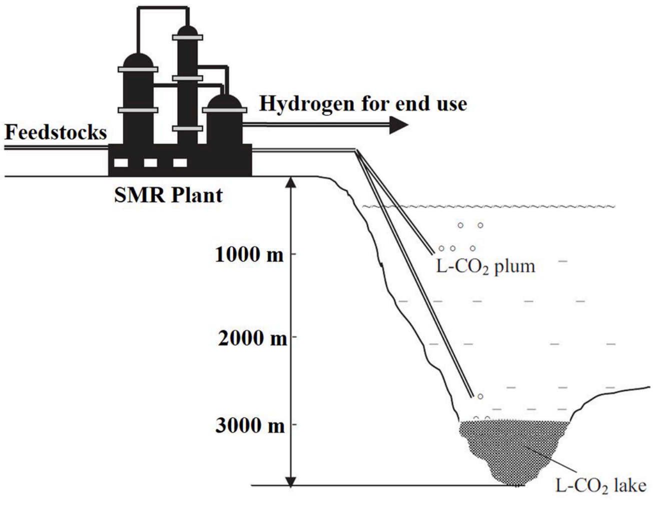


Fig. 22. H_2 production via SMR process and CO_2 sequestration options [344].

Apart from the CCS technologies for carbon free energy supply, the captured CO_2 can also be utilised as raw materials in several industries. The technology that assesses the quality of produced CO_2 from various sources and reprocessing [312,365,366] the CO_2 into usable feedstock for respective industries is known as the carbon capture and utilization (CCU) process. Ho et al. [366] observed that the established CCU technologies require a highly purified and uniformly pressurised CO_2 supply in order to use that as feedstock in the respective industries. These authors have reviewed various publications and listed various sources of CO_2 gas along with its percentile quantity of purity (varying between 7.4% and 90%) in the emitter gas mixtures. The carbonated beverage, enhanced coalbed methane recovery, methanol, methane, refrigerant, and decaffeination agent require 99% pure CO_2, while the required pressure can vary from 0.04-300 bar atmospheric pressure condition as per the respective process requirement. On the other hand, enhanced gas recovery, urea production and mineral carbonation require 99.9% pure CO_2 with pressures ranging between 1 and 150 bar atmospheric pressure. Moreover, CO_2 can also be used at atmospheric pressure in various industries. Pure CO_2 obtained through the CCU technologies integrated with the plastics (e.g., polycarbonate production) industry [367], petrochemical (e.g., methanol, methane) synthesis industry [368,369], biofixation of CO_2 though microalgae cultivation [370,371] with the potential of developing biorefineries, building materials and carbon fibre industries [372,373] all use atmospheric pressurised CO_2. Purification and pressurization of CO_2 feedstock to a reprocessing industry may cost about 70-75% of the overall process where this raw material is used, but it is highly essential to valorise this compound to establish circular economy [374,375]. With proper CCU policies, the circular economy market may grow to 700-800 billion USD by 2030 which may consume about 15% of the present worldwide annual CO_2 emissions [373].

Carbon dioxide from atmosphere can also be used to produce e-fuel with hydrogen and the e-fuel can be used in transport sector such as vehicle in road, ship in sea, and airplane in air. The produced e-fuel is carbon neutral because it will release the carbon during the combustion which is captured to produce e-fuel. So, the overall carbon di-oxide in the atmosphere will not be increased due to combustion of e-fuel and hence the e-fuel can be termed as carbon neutral which can solve the issue of hydrogen storage partly [376] .

5.4. Energy conversion and storage development

Public and private sector should focus on the development of hydrogen storage because hydrogen economy cannot progress without proper hydrogen storage. The International Energy Agency (IEA) Hydrogen TCP consists of 31 members including 23 countries, the United Nations Industrial Development Organization (UNIDO), the European Commission, and 6 sponsors. The ongoing task of the IEA Hydrogen TCP is to develop reversible or regenerative hydrogen storage materials. An IEA Hydrogen TCP task force identifies that storage capacities and operating temperatures depend on the application types such as mobile systems, transport and delivery stations, or storage systems. The development of improvement of materials is linked with the understanding of hydrogen storage mechanism. Fig. 24 shows the mechanism of hydrogen storage development [377].

The main challenge of hydrogen after production is storage and transport. Hydrogen has very low boiling temperature which makes it difficult to store. After storing hydrogen for long time at low temperature, the container material degrades and make it difficult for further storage. The research and development of storing hydrogen as liquid organic hydrogen carriers (LOHCs), metal alloy hydrides, and liquid ammonia is on. If a suitable solution of storing hydrogen is found, then the hydrogen will jump a big leap in its way to be the alternative of fossil fuel.

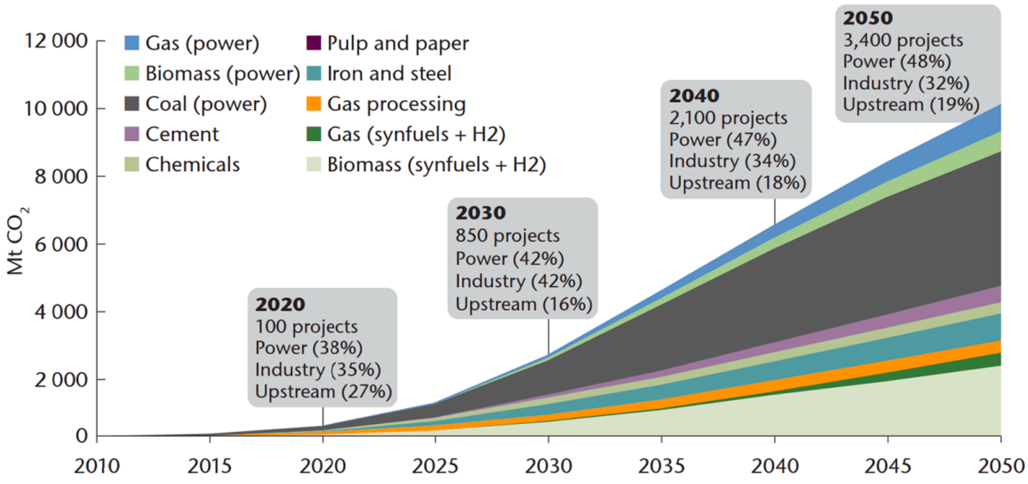


Fig. 23. Projection of global CCS deployment projects by 2050 in various energy sectors [358].

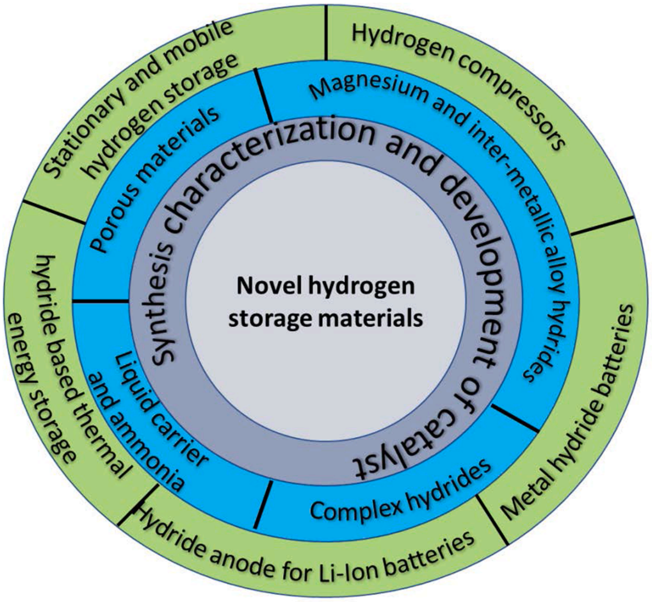


Fig. 24. Development strategy of hydrogen energy storage and conversion using reversible or regenerative hydrogen storage [377].

6. Applications of hydrogen in different sectors

There are extensive use of hydrogen as raw material for fertiliser production (i.e., ammonia (NH_3) production), petroleum refineries, methanol (CH_3OH) production, reducing agent for metal (steel, aluminium) ore processing and manufacturing of glass, hydrochloric acid (HCl) production, food industries (e.g., hydrogenation of oils or fats), atomic hydrogen welding (AHW), coolant, hydrogen peroxide (H_2O_2), analytical chemistry (e.g., atomic absorption spectroscopy, gas chromatography), aerospace, electronics (semiconductors), weather balloons, and fuel for rockets as well as the transport industry (e.g., fuel cells, and liquid hydrogen combustion) [332,378-380]. In transport sector, hydrogen will be used in hydrogen fuel cell and in internal combustion engine but in energy sector, hydrogen will be used as energy carrier. Capital costs, operating costs, infrastructure requirements, range to refuelling, refuelling facilities, refuelling time, safe life expectancy of alternative options, emissions, space restrictions, and overall safety concern are the key factors to facilitate the implementation of hydrogen fuel as an alternative fuel for the transport sector [318,381,382]. The performance of the hydrogen systems in the transport sector is presented in Table 15.

Source: Technology Roadmap Hydrogen and Fuel Cells [382].

The cost of fuel cell is higher as compared with the vehicle with ICE. The lifetime of fuel cells is only 150000 km with a cost of $60-100k. People will not buy the FCEV unless the price is reduced, and the lifetime is prolonged. Therefore, there is little chance of replacing ordinary vehicle with the fuel cell vehicle very soon.

6.1. *Hydrogen as fuel in internal combustion engines*

Hydrogen can be used directly or as a mixture with fossil fuels into the internal combustion engine. The application of hydrogen into the internal combustion engine requires the hydrogen storage and transmission. Moe research of hydrogen in internal combustion engine is needed to investigate the characteristic of hydrogen combustion in ICEs. Peeters [383] has investigated the performance of hydrogen in ICE using CFD modelling. He found that the combustion is very fast and severe because of high flame speed when hydrogen was used and hence the pressure peaks is high with low thermal efficiency. He suggested and found that by optimising the hydrogen injection, combustion can be slowed down, resulting in lower pressure peaks, lower NOx emissions and higher power outputs can be achieved. Shi et al. [384] conducted CFD simulation with hydrogen-enriched fuelled into proposed

Table 15
Performance of hydrogen systems in the transport sector [382].

Application	Capacity	Energy efficiency*	Investment cost**	lifetime	Maturity
Fuel cell vehicle	80-120 kW	Tank to wheel 43-60% (HHV)	$ 60 K-100 K	150,000 km	Early market
Hydrogen retail station	200 kg/day	-80% inc. compression to 70 MPa	$1.5-2.5 M	-	Early market
Tube trailer (gaseous)	Up to 1000 kg	-100% (without compression)	$1M ($ 1000 per kg payload)	-	Maturity
Liquid tankers	Up to 4000 kg	Boil-off stream: 0.3% loss per day	$ 75 K	-	Maturity

- Lower heating value*, $=USD
- All power specific investment costs refer to the energy output**
- HHV-higher heating value

modification of rotary engine by configuring the turbulence-induced-blade (TIB) and observed that NOx emissions can be reduced with trailing TIB while the combustion is better in leading TIB. Hence the authors have proposed for more parametric investigations to find out the optimised operating conditions for hydrogen enriched combustion along with minimal NOx emissions.

Traditional internal combustion engines can be customised to operate on pure hydrogen (‘HICEs’) and may possibly see early implementation because they are significantly less expensive than fuel cells. Hydrogen can be used all types of internal combustion engines. Besides, the HICEs can adopt all the available advanced automotive engine combustion technologies like direct injection (DI), turbocharging, pre-chamber ignition, Miller cycle, lean combustion, cylinder deactivation, start-stop of the engine, and modern transmission system advancements which have proved significant improvement in reducing emissions while reducing fuel consumption [385]. The release of NOx and lower fuel efficiency (~30%) for combustion of hydrogen in the ICEs may impede the acceptance of HICEs for long term usage in transport [118]. But, various exhaust treatments like exhaust gas recirculation (EGR) [386,387], leaner NOx trapping with 3-way catalytic converter (TWC) [388,389], selective catalytic reduction (SCR) [390,391], and pre-intake as well as in-cylinder control strategies [386] can effectively help to reduce NOx emissions from a HICEs. Hydrogen can be mixed with diesel in dual-fuel vehicles or natural gas (‘hythane’) or in bi-fuel to switch between them. The retrofitting of hydrogen into the existing engine will permit the use of the present infrastructure available. Although the blending of hydrogen is not a net-zero emission outcome, it is an option to lower carbon emissions [381]. The benefits of the addition of H_2 can be summarised as follows [317]:

- Enhance fuel octane number.
- Engine performance increases with the increase of octane number.
- Engines size can be reduced with more efficient.
- Facilitates ultra-lean burn.
- Up to 30% increase of engine efficiency.

The stoichiometrically calculated air-fuel ratio (A/F ratio) for the hydrogen combustion engine is almost 34.3:1 (w/w) (2.4:1 v/v), whereas, the gasoline engine is 14.7:1 (w/w) and a diesel engine is 14.5:1 (w/w) [77]. Due to diverse flammability, hydrogen can burn at a higher A/F ratios like 180:1 as well [77]. This indicates that more air is required to burn the amount of hydrogen drawn into the combustion chamber than for other vehicular fuels. At stoichiometric combustion conditions, 2 moles H_2 and 1 mole O_2 are required to generate 2 moles H_2O to produce about 0.572 mega joules (MJ) of energy [392]. Table 16 briefly presents the amount of hydrogen being drawn into the combustion chamber at various metering conditions, i.e., gaseous hydrogen at normal pressure, liquid hydrogen and very highly compressed (~70 MPa bar) hydrogen in comparison to the standard percentile energy production of gasoline combustion. Volumetrically at normal gaseous condition, about 29.6% hydrogen occupies the combustion chamber in comparison to that of 1-2% for gasoline [185] as calculated in Eq. (35). The density (kg/m^3) of hydrogen varies with the applied pressure, e.g., 0.0838 kg/m^3 (1 atm), 23.65 kg/m^3 (35 MPa), 39.69 kg/m^3 (70 MPa) and 72.41 kg/m^3 (liquified) [393]. On the other hand, the densities of gasoline, diesel, LPG and natural gas are about 745 kg/m^3, 845 kg/m^3, 541 kg/m^3, and 0.77 kg/m^3 respectively at normal temperature and pressure (STP) [393]. While comparing the density of the fuels, hydrogen demonstrates better efficacy in terms of energy production per unit weight equivalent to the gasoline fuel. It also shows that, to gain more energy efficiency from combustion of hydrogen fuel in the internal combustion engines, highly compressed hydrogen offers higher energy efficiency as shown in Table 16.

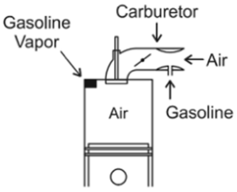
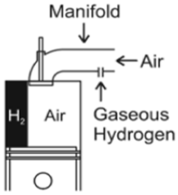
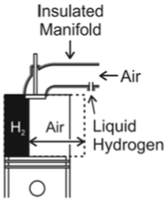
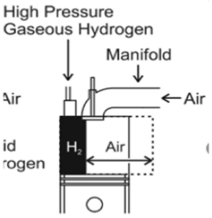
$$\%H_2 = [volume_{H_2}]/[(volume_{air} + volume_{H_2}) = [2/(4.762+2)] \times 100\% = 29.6\% \quad (37)$$

E-fuel can be an alternative fuel to internal combustion engine which can be used in transport sector such as road vehicle, aviation, rail, and sea-transport. E-fuel can be produced by trapping the CO_2 from atmosphere or emission from industry to produce oligomeric oxy-methylene dimethyl ether (OME). Sai et al [376] suggested that E-fuel produced using the mechanism Fischer Tropsch reaction can alleviate the issue of storing hydrogen. The authors also presented a comparative analysis of combustion in ICE of OME1 fuel blended with diesel with that of the diesel and other fuels. They found that the OME blended with diesel has favourable characteristic such as less soot production. Although there is less maximum rate of energy conversion due to low energy density of e-fuel, this can be overcome by mixing with high energy density fuel.

6.2. *Hydrogen fuel cells in vehicles*

Hydrogen can be used in hydrogen fuel cell to produce electricity and this electricity can used in different applications such as electric vehicle and industry and domestic uses. The fuel cell can be installed in vehicle and produce electricity to run the vehicle. Fuel cells are considered for use in fuel cell vehicles and fuel cell systems are for stationary application in large central power stations and distributed power generators. This system can be used for residences and buildings in urban and remote areas [128]. Power plant companies are exploring the usage of solid oxide fuel cells (SOFCs), phosphoric acid fuel cells (PAFCs), and molten carbonate fuel cells (MCFCs) [128]. Central power plants use the higher temperature fuel cells (MCFCs and SOFCs) and the smaller power generators mainly use polymer electrolyte fuel cells (PEFCs) for residential units and in automobiles for propulsion power. A comparison of emissions from BEV (Battery electric vehicle), FCEV (Fuel cell electric

Table 16
Comparison of volumetric efficiency and energy output between gasoline and hydrogen fuelled engines [77].

Types of fuel	 **Liquid Gasoline**	 **Gaseous Hydrogen Pre-Mixed**	 **Liquid Hydrogen Pre-Mixed**	 **High Pressure Gaseous Hydrogen Injection**
Fuel	17 cc	300 cc	405 cc	420 cc
Air	983 cc	700 cc	965 cc	1000 cc
Energy (%)	3.5 kJ (100)	3.0 kJ (85)	4.0 kJ (115)	4.2 kJ (120)

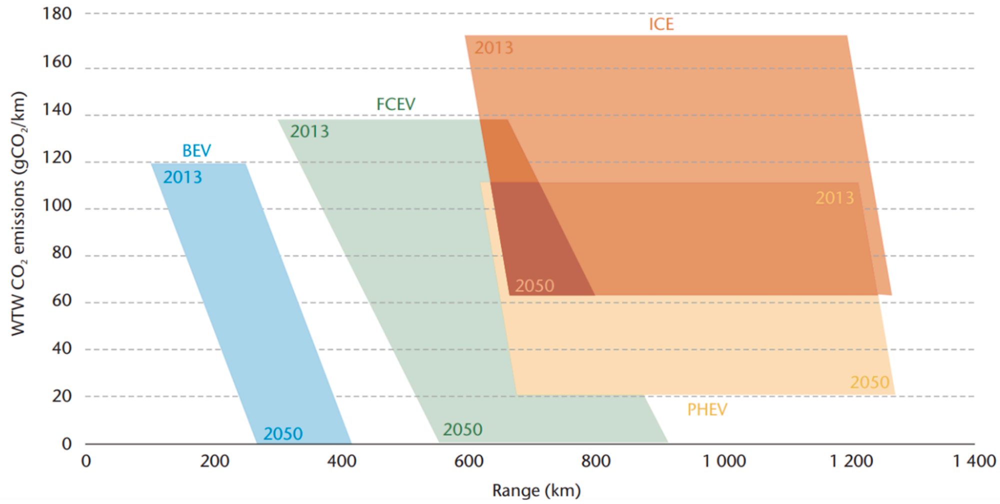


Fig. 25. Comparison of emissions for different vehicle [377,382].

vehicle), plug in hybrid vehicles (PHEVs), and ICE vehicles is presented in Fig. 25.

Fuel cell can be a good option to use hydrogen to generate electricity which can be used to run the vehicle as electric vehicle. Unlike hydrogen combustion in ICE, hydrogen can be used to generate electricity using different types of cells. Using hydrogen in fuel cell will help reduce the emission into atmosphere and fulfill the goal of carbon neutral in 2050. To get traction in the market, the price, durability and availability of fuel cell must be arranged. Not many car makers are manufacturing the fuel cell vehicle and the vehicles are not easily available worldwide. Currently, BEV and hybrid car is available in the market but no car with fuel cell is readily available in the market.

6.3. Other progressive industries

Hybrid systems which consist of hydrogen technologies (fuel cells, hydrogen stores, and electrolysers), integrated with battery or wind/ solar power backup, are recommended to fulfill the growing demand for power in telecom base stations in rural and remote areas [394]. The hybrid systems can meet the demand of growing power in the telecom system by shipping hydrogen to remote areas.

Hydrogen can be mixed or injected into the gas network safely with small quantities because the safe amount of hydrogen is limited by administrative and technical constraints [118,395]. Hydrogen has a lower energy density than methane, as a result, a 20% blend of hydrogen with natural gas is equivalent to 7% hydrogen by energy content. The energy content of hydrogen (E_H) is estimated using the volume or mole fraction of methane (V_M) and hydrogen (V_H) as in Eqn. (38).

$$E_H = \frac{11.88V_H}{11.88V_H + 39.05V_M} \tag{38}$$

where 11.88 is the volumetric HHV (MJm^{-3}) energy content of hydrogen and 39.05 is the volumetric HHV (MJm^{-3}) energy content of methane [393], and $V_M = 1 - V_H$. From Fig. 26 it can seen that mixing of 20% hydrogen by volume will save 13 gCO_2 per kWh [118]. Various issues must be considered to evaluate the safety matters linked with mixing hydrogen into the present natural gas pipeline network to be used at the consumer end [118,395].

Hydrogen can used with the existing fuel such as natural gas and transmitted through natural gas network by mixing with them with certain proration. Due to policy and regulation for safety, there are limitation of hydrogen amount to mix with natural gas. Mixing hydrogen with natural gas will save carbon emission into the atmosphere. Netherlands and Germany are using high volume of hydrogen into the grid and other country should follow their footsteps to increase the percentage hydrogen in the grid.

7. Economic analysis of H_2

The cost of producing hydrogen gas through a specific process is the combination of investment expenditures, operation expenses, and maintenance costs. The factors involved in the cost of hydrogen are

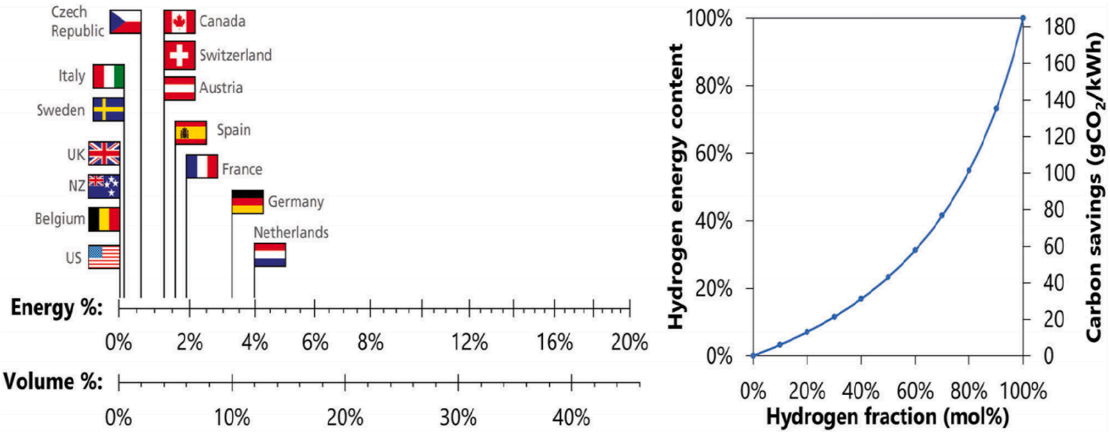


Fig. 26. (a) Percentage of Hydrogen in the grid around the world; and (b) Hydrogen fraction, energy content and carbon saving [118].

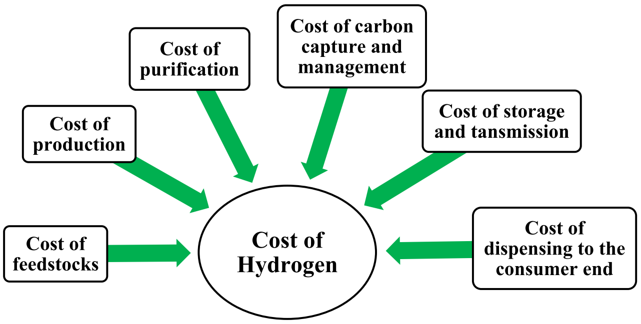


Fig. 27. Factors involved in overall cost of hydrogen for the consumers, redrawn from ref [396].

presented in Fig. 27.

With Biogas as feedstock for hydrogen production, if the payback period is considered as equivalent to 8 years of production period, it may cost about 0.27 US$/kWh [397]. Wang et al. [398] have carried out techno-economic (i.e., energy efficiency, capital investment expenditures, consumption of raw materials, costs related to regular production and cost incurred due to carbon emission or management) performance analysis between coal-to-hydrogen (CTH) processes and biomass-to-hydrogen (BTH). Both the CTH (37.82%) and BTH (37.88%) have comparable energy efficiency. The BTH process has about 70.92% more material consumption than that of CTH (6.43 tonnes/tonnes of H_2) for production of per tonne of hydrogen gas which indicates the possibility of higher CO_2 emission from the BTH process. In fact, the BTH process emits about 6.7% less CO_2 than that of CTH (16.39 tonnes CO_2-e/tonne of H_2) due to the variation of composition of the raw materials. However, the higher raw material costs of the CTH process (51.4% of total production expenses) can make the BTH process (44.7% of overall production cost) competitive enough to be chosen for industrial development. From another point of view, biomass resources could be mainly consisting of green wastes, but coal mining is related to fugitive emissions as well in addition to its own carbon content emission during the hydrogen production process. The total capital investment cost of the BTH process was 19.24% higher than that of CTH (141.8 M US$). Both the processes have very high amounts of energy losses which need to be improved. In the case of hydrogen gas recovery and purification from the mixture of gases, the cost of the PPU is linked to the efficiency of the hydrogen production process [302]. When biomass gasification is performed, the steam to biomass ratio (S/B) variation between 1 and 1.5 in addition to the remarkable reduction of PPU cost can lead to fluctuation of H_2 gas in a decentralised station of about 12.75-9.5 €/kg [302]. The cost of production of hydrogen using different methods are presented in Table 17. The lowest production cost per kg of hydrogen is CG without CCS and the highest is photo-electrolysis. The highest capital cost is nuclear thermolysis and the lowest is biomass pyrolysis.

The techno-economic analysis of ALK and PEM electrolysers is presented in Table 18. The efficiency of ALK and PEM are almost similar. The total system cost of ALK is lower than that of PEM, but the system lifetime is same.

Many factors contribute the cost of hydrogen which includes the feedstock, production, storage, distribution, transmission, and other factors as can be seen in Fig. 27. The crucial challenge for hydrogen is to reduce the price of the hydrogen. The highest cost of hydrogen is the hydrogen from SMR with CCS. The low-cost hydrogen can be produced from CC with CCS, CG without CCS and indirect bio-photocatalysis. Nuclear thermolysis is the most expensive to install to produce hydrogen and the cost of hydrogen is $2.17-2.63 per kg of hydrogen. The cost of hydrogen from electrolysis process is costlier than other process but the positive side of electrolysis process is that they use water as feedstock. ALK and PEM electrolyser are also used for hydrogen production, and they are in commercial sate. SO is still in research and development stage but has high possibility of improvement with lower capital cost.

Table 17
Comparison of cost of production of hydrogen with different methods [399].

Process	Energy source	Feedstock	Capital cost (M$)	Hydrogen cost ($/kg)
SMR with CCS	Fossil fuels	NG	226.4	2.27
SMR without CCS	Fossil fuels	NG	180.7	2.08
CC with CCS	Fossil fuels	Coal	545.6	1.63
CG without CCS	Fossil fuels	Coal	435.9	1.34
ATR of methane with CCS	Fossil fuels	NG	183.8	1.48
Methane pyrolysis	Internally generated steam	NG	–	1.59–1.70
Biomass pyrolysis	Internally generated steam	Woody biomass	53.4–3.1	1.25–2.20
Biomass gasification	Internally generated steam	Woody biomass	149.3–6.4	1.77–2.05
Direct bio-photolysis	Solar	Water+ algae	50 $/m^2	2.13
Indirect bio-photolysis	Solar	Water + algae	135 $/m^2	1.42
Dark fermentation	–	Organic biomass	–	2.57
Photo-fermentation	Solar	Organic biomass	–	2.83
Solar PV electrolysis	Solar	Water	12–54.5	5.78–23.27
Solar thermal electrolysis	Solar	Water	421–22.1	5.10–10.49
Wind electrolysis	Wind	Water	504.8–499.6	5.89–6.03
Nuclear electrolysis	Nuclear	Water	–	4.15–7.00
Nuclear thermolysis	Nuclear	Water	39.6–2107.6	2.17–2.63
Solar thermolysis	Solar	Water	5.7–16	7.98–8.40
Photo-electrolysis	Solar	Water	–	10.36

Table 18
Techno-economic analysis of ALK and PEM electrolysers [326].

Technology	ALK		PEM	
Year	2017	2025	2017	2025
Efficiency, kW /kg of H_2	51	49	58	52
Efficiency (LHV) %	65	68	57	64
Lifetime stack Operating hours	80,000 hr.	90,000 hr.	40,000 hr.	50,000 hr.
CAPEX-total system cost (inc. power supply and system costs) €/kW	750	480	1200	700
OPEX % of initial CAPEX/Year	2%	2%	2%	2%
CAPEX-Stack replacement €/kW	340	215	420	210
Typical output pressure kPa	Atmospheric	1500	3000	6000
System lifetime Years	20		20	

8. Technology and commercial readiness of H_2 production

Technology readiness levels (TRLs) and Commercial readiness indexes (CRIs) are two globally accepted benchmarks that express the maturity of technologies. TRLs elaborate the growth and continuing development of a particular technology through the initial phases of the innovation chain and CRIs provide a ranking to evaluate industrial

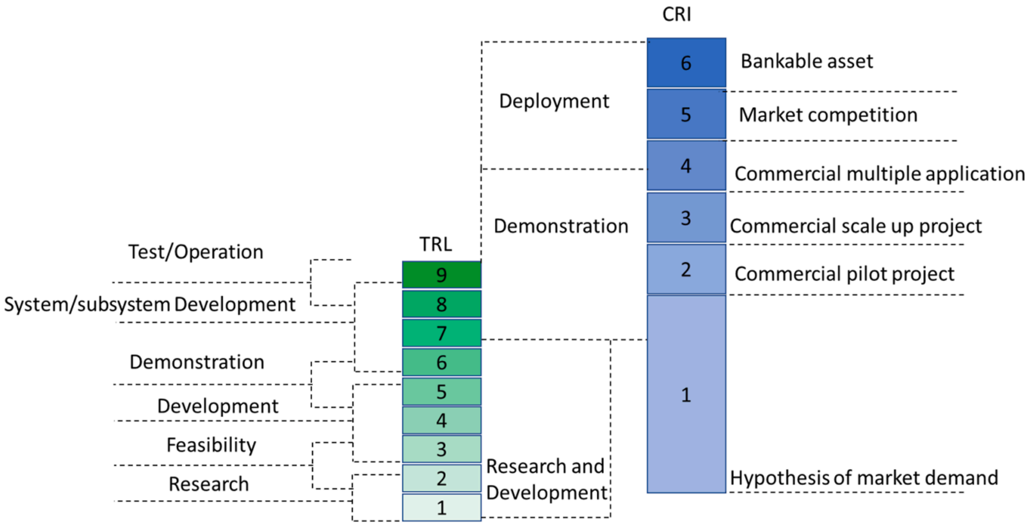


Fig. 28. TRL and CRI levels, redrawn from ref [343].

Table 19
Recent status of key technologies for hydrogen generation [343].

Applications	Capacity	Efficiency	Initial investment cost	Lifetime	Maturity
Large scale SMR	150-300 MW	70-85% (LHV)	400-600 USD/kW	30 yrs.	Mature
Small scale SMR	0.15-15 MW	~51% (LHV)	3000-5000 USD/kW	15 yrs.	Demonstration
AE electrolyser	Up to 150 MW	65-82% (HHV)	850-1500 USD/kW	60,000-90,00 hrs.	Mature
PEM electrolyser	Up to 150 MW (stacks), and up to 1 MW	65-78% (HHV)	1500-3800 USD/kW	20,000-60,000 hrs.	Early market
SO electrolyser	Lab scale	85-90% (HHV)	-	~1000 hrs.	R&D

Table 20
TRL of different hydrogen production process [400].

Hydrogen production technologies	TRL	Feedstock
Alkaline electrolysis	9	H_2O + electricity
PEM electrolysis	7–8	H_2O + electricity
Solid oxide electrolysis	3–5	H_2O + electricity + heat
Biomass gasification	4	Biomass + heat
Biological	1–3	Biomass + microbes (+ light)
Photoelectrochemical	1–3	H_2O + light
Thermochemical	1–3	H_2O + heat

barriers and risk which facilitates funding decisions to decrease risks and impediments at the different phases moving towards commercialization. When a technology attains the demonstration and implementation level, then a set of separate elements are introduced to help in determining the commercial readiness of a technology or project. Details of the TRLs and CRIs are presented in Fig. 28 [343].

Applications and the status of different technologies are presented in Table 19. The technology readiness levels of different production processes are presented in Table 20.

SMR process has the highest lifetime than that of the other technology. This technology requires less initial investment than other technologies. SMR technology is not completely sustainable process because it produces CO_2. AE and PEM electrolysis technology is expensive as compared to SMR. AE is matured technology but PEM and SO is in nascent state in the technology readiness level. Electrolysis processes use water as their feedstock which is renewable, abundant, and does not produce GHG therefore this process can be termed as sustainable if the energy is taken from renewable sources such as wind and solar. Among all technology presented in this study, Alkaline and PEM is at the top of the TRL chart as shown in the Table 20 but more research is needed to reduce the initial cost and the durability of the process.

9. Discussion and challenges for hydrogen

Although hydrogen has huge potential to replace conventional fossil fuels, there are many challenges that need to be addressed so that process evolves smoothly. This section has presented the current challenges for hydrogen as a replacement to existing fuels.

Current capability of hydrogen production, storage and supply worldwide is far less than what will be required in future [401]. Hydrogen related infrastructure including production, storage, and delivery to end users must be developed based on the demand. The infrastructure for hydrogen transportation, storage and delivery are not fully developed anywhere in the world to cope with the demand that will arise when vehicles are progressively converted to be powered by hydrogen fuel or fuel cells. There are very limited numbers of hydrogen refuelling stations worldwide as compared to conventional fuel stations.

Current hydrogen storage systems are not adequate to meet the demand for the weight and volume of storage of hydrogen which are high as compared to conventional vehicle fuel storage, so novel hydrogen storage development is imminently required. Ammonia can be a good carrier for hydrogen, but the ammonia-based energy system has many challenges to face. Ammonia is produced worldwide using fossil fuels and, as a result, production of carbon-free ammonia by synthesis is a difficult area which needs extensive research and renewable energy utilization in a suitable way can assist to solve this issue [402]. The sustainability of ammonia should be measured to identify the applicability of ammonia as developed by Liu et al [402]. However, current research and development in this area have mainly been aimed towards the improvement of small and medium size devices such as reciprocating engines. In addition to that, toxicity of ammonia is another major barrier which is holding back the application of these technologies [342].

Cost of hydrogen is another factor that needs to be addressed to make hydrogen a viable alternative to fossil fuels. The price of hydrogen is higher than that of conventional fuel, so it is critical that it be reduced. Hence factors that contribute to the overall price must be improved such as the development of efficient and low-cost solar energy production.

Public acceptance and awareness are other issues that can impede the use of hydrogen. For any technology to flourish, it first needs to be accepted by the general community. This will require a rigorous public awareness program, and this must include details of the relevant health and safety analysis as well as a review of legislation so that all these issues are able to be addressed.

Hydrogen related techno-economic feasibility is a big challenge for hydrogen. The affordability of the technology of green hydrogen production is another factor. The cost of the integrated system that will produce the green hydrogen should be within the reach of the potential users within the community.

Agyekum et al [403] reviews the hydrogen production and identified the factor affecting their scale up. They identified, storage and transportation of hydrogen, high cost of production as factor affecting their scale up and role in future energy which has been mentioned above. In addition to that, they also identified that the absence of a value chain for clean hydrogen, lack of international standards, risks in investment, and flammability are factor that affecting their scale up and role in future energy.

10. Conclusions and recommendations

This paper presents and discusses hydrogen as energy carrier by considering various aspect of hydrogen such as production, storage, transmission, and distribution. Literature reviewed indicates that hydrogen has been used in different sectors for a century and recently the application of hydrogen as a fuel or energy carrier has gained momentum due to the concern of global warming and greenhouse gas emissions which produce adverse effects on the climate. To produce hydrogen, different energy sources can be used including renewable energy, natural gas, oil, nuclear energy, and coal but to claim green hydrogen the whole process of production should be carbon neutral. Hydrogen gas can be transported by pipelines and liquid hydrogen can be transported by ships, but a complete network of hydrogen transmission, storage, distribution, and delivery is very important to meet the global demand which is long way to achieve. Hydrogen can be used to produce electricity and can be transformed into methane. Methane can be used for domestic power and as feedstock for industry and used directly as fuel in vehicles and planes. Many countries have invested billions of dollars in this field to produce green hydrogen but still need more funding and support from government to achieve 2050 carbon neutral goal.

The cost of hydrogen is expected to reduce to the desired 1-2 \$/kg of H_2 from current 4-7 \$/kg H_2. Hydrogen has the best energy-weight ratio 120-142 MJ/kg among all conventional fuels. Among all hydrogen production process, SMR process has about 48% share of global hydrogen production with highest efficiency of 70-85% with lowest production cost. Solid oxide fuel cell (SOFC) technology of hydrogen conversion and storage has highest efficiency of around 70% but this technology is in demonstration stage. Metal hydride storage system cost less (125 $\$/m^3$) as per specific volumetric cost and ammonia has lowest specific energy cost (13.3 \$/GJ) among all storage system.

A widespread application of hydrogen as fuel for the transport sector and as feedstock for the chemical industry is imminent and to cope with this expected future demand, a complete infrastructure of hydrogen from production to delivery is needed. Different countries are formulating policies and enacting laws to include hydrogen as fuel in the transport and energy sectors to achieve net-zero emission within a decade and hence more research and development funds are needed in this field. Technological advancement of hydrogen production, storage, distribution, and transmission is essential which needs support from government.

More research is needed to make hydrogen versatile and available worldwide to be used in different sectors as an alternative to conventional fuels. These include, but are not limited to, low-cost and efficient solar energy production for hydrogen, nanoscale catalyst development, development of novel hydrogen storage materials, low-cost and durable cathodes in fuel cells at low temperature, and a thorough study on hydrogen safety.

The following research should be carried out in the near future;

- Maturity of hydrogen conversion technology.

Many technologies available for hydrogen production such as PEM and SO are in an initial stage or in the pilot scale. More research is needed to scale up production into industrial scale which can bring down the cost of hydrogen.

- Transition of ICEs from fossil fuel to hydrogen fuel in vehicles.

ICEs are mainly designed to run with fossil fuels as a result hydrogen in ICEs poses many challenges which opens opportunity to carry out research in this field. Among the challenges, the crucial points to note are back-fire, low output power, high NOx production, pumps capable of delivering liquid hydrogen, spark plug to deal with hydrogen, and electrode compatible with hydrogen. Most of the research is focused on the hydrogen production and virtually no research and development have been carried out to design the ICE suitable for hydrogen fuel. Therefore, research should be focused on the compatibility of ICE or new design of ICEs to suit the hydrogen fuel from the storage tank in vehicle to the combustion chamber in engine.

- Reduction of production and delivery cost of hydrogen.

The overall cost of hydrogen is higher than that of the fossil fuels. More search is needed to innovate the low-cost production of hydrogen and delivery. The cost of production of hydrogen is currently in the range of \$4-7/kg H_2 excluding the cost of network and delivery system. The delivery system requires high pressure compressor, storage tank and colling system. To bring the price down, more research is needed around low-cost and efficient separation and purification, development of catalyst for low temperature, durable and less expensive membrane, develop low cost photocatalyst and electron transfer catalyst.

- Reduction of cost of fuel cells and enhance their performance.

Different types of fuel cell have different shortcomings which need to be overcome. For automotive application, the power density of fuel cell needs to improve. The cost of fuel cells is higher compared to ICE as well as the durability is less than that of ICE. The cost of fuel cells come from the expensive material used as well as the production of fuel cell stack. The chemical stability and conductivity should be improved to enhance the durability and performance of the fuel cell.

- Overcoming the shortcomings of hydrogen storage.

The main challenge of hydrogen as a substitute fuel is storage. Hydrogen needs extremely low temperature to store which make it difficult to store, carry and deliver. Novel storage technology is imminent to develop. Research should be carried out to develop novel storage devices to cope with the challenging of hydrogen storage.

- Developing infrastructure to cope with hydrogen transport, distribution, and storage.

The current infrastructure around the globe is not sufficient to cope with the overall energy demand in the world. Hence, worldwide network of hydrogen is important to meet the demand around the world. There are no details outline as well as the infrastructure for hydrogen transport, distribution, and storage. More research should be carried out for the development of efficient transport, distribution, and storage.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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