Sustainable Synfuels in Carbon Neutral Energy Industry

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Cambridge
Scholars
Publishing

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This book first published 2025

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN: 978-1-0364-4690-1
ISBN (Ebook): 978-1-0364-4691-8

This book is dedicated to my wife Mary and three sons James, Jonathan and Keith

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PREFACE

The energy industry is changing and evolving in many different directions. While there are several reasons for this paradigm shift, the most important reason is the realization that carbon emissions caused by fossil fuels are causing global warming and the effects on unpredictable and harmful behavior of the environment. There is also a realization that fossil fuels are non-renewable and have a limited life span. For these reasons, the world has come to realize that energy needs to be harvested from other renewable sources like wind, solar, geothermal, hydro, biomass, waste, and hydrogen along with more emphasis on nuclear energy which causes less emission of carbon. Carbon dioxide should also be utilized to generate energy and fuels to make the energy industry carbon-neutral or negative. There is also a realization that the future energy industry must provide energy and power to more than a billion people who have no access to such a need. As the population of the world grows and the need for economic development of the developing nations increases, the provision of secure and stable energy which is environment friendly and economical has become more of a necessity. Going forward, to protect the environment, biomass, water, and CO2 should be the major sources of future fuel needs.

The energy industry of the future must bring about two major paradigm shifts; an increasing role of renewable, hybrid, and distributed electricity and the use of biomass, water, and CO2 for sustainable carbon-neutral or carbon-negative fuels. While the role of electricity is bound to increase due to the explosive growth of digitalization, IoT, and the technological explosion of portable electronics, computers, etc., the sources of electricity generation must change. It is now well-accepted that electricity will be the major energy vector of the future. As shown in my previous two books, power generation without carbon emission would be the major research and development direction for the future. Along with power generation, more efforts will be made to store and transmit power. Electric transportation may be a new reality. Power must however come from renewable sources rather than fossil fuel. This shift in sources will make power more hybrid and distributed. Unlike fossil fuel sources, renewable sources are more distributed in nature and they can be harnessed at local levels without centralized infrastructure. Distributed energy systems are more flexible, easily moveable, and best for residential and transportation energy needs. Furthermore, renewable and distributed sources are better implemented with the help of new smart grids which provide two-way communication between suppliers and customers. Distributed energy infrastructures such as microgrids, and nano grids are safer and less vulnerable and are more protected from major catastrophes, cyber threats and environmental mishaps than utility grids. Small-scale nuclear energy systems can be less threatening than large-scale systems for nuclear accidents. The economy of scale in distributed systems can be handled by the modular approach which is easy to install and remove. To support renewable power, the power grid will become hybrid. The grid of the future will contain power from dispatchable and non-dispatchable sources like solar and wind energy. While hybrid power will provide more flexibility and security, it will also result in a more complex management system at the local level.

The second major change in the energy industry will be the change in the feedstock for required fuels. The present book addresses this major change in sustainable fuels for the future energy industry. Unlike fossil energy-based synthetic fuels used at present, the sustainable fuels of the future must come from biomass, water, and CO2. These green fuels will be generated by several electrochemical and photo-electrochemical systems besides conventional thermochemical, biochemical, and reforming systems. Besides providing heating and cooling needs, these fuels will provide energy carrier needs for long-distance transport as well as energy storage for the long -term needs. The most important synfuels in the carbon-neutral energy industry will include hydrogen, ammonia, syngas, methanol, and several biofuels such as biogas, bio-ethanol, bio and renewable diesel, and sustainable aviation fuel. The present book examines these fuels in detail.

Along with the electrical economy, the hydrogen economy is essential for the decarbonization of the energy industry. Hydrogen is an energy carrier with a wide range of properties to be used as fuel; as raw material or as an interface between electricity and various chemical energy forms through the power-to-gas process. There, it can be used as a storage medium to absorb the renewables fluctuations and/or as feedstock for synthetic natural gas production through methanation reaction, with the key feature of offering a complete carbon emission-free pathway. Its high content of energy per mass (higher heating value 142 MJ/kg), is around three times larger than common fossil-derived fuels, namely natural gas (53.6 MJ/kg), diesel (45.4MJ/kg) and gasoline (46.4MJ/kg). Additionally, its capability to decarbonize some chemical processes and provide the fuel for the transport sector, makes hydrogen a key energy carrier to alleviate the current energy and environmental challenges. Hydrogen and its several derivatives will be very important for the storage and transport of electric power as well as supplying energy for heating and cooling needs and thus they will be the major vectors supporting the energy and chemical needs of the world.

Some now argue that a true decarbonized energy industry cannot be achieved without the use of hydrogen for energy, chemicals, and food. The European Commission is particularly determined to make Europe deliver on its ambitious climate promise to achieve carbon neutrality by 2050. One of their main strategies is to fully develop a hydrogen economy and apply it to all major sectors of the economy. While currently, natural gas is the primary source of hydrogen production, in the future, water may be an inexhaustible source of hydrogen. Hydrogen transportation from the production site to the consumption site is a vital process in the hydrogen production economies because it can increase production costs, influencing its affordability. Hydrogen storage is considered an urgent and challenging stage because it helps develop safe, reliable, efficient, and adequate global storage and transport mechanisms for renewable electricity. Unfortunately, the use of hydrogen vectors alone as an energy and chemical carrier has some deficiency that requires other hydrogen-derived vectors. In this respect, four other chemical energy vectors are considered to be very important. They provide significant supporting roles to hydrogen as a chemical intermediate and energy vector. These four vectors are syngas, ammonia, methanol, and biofuels. This book examines the value of these four vectors along with hydrogen to the energy and chemical industries.

Syngas is one of the important intermediate and chemical energy vectors because it can produce a variety of chemicals and synthetic fuels. In the past, the majority of syngas have been produced using fossil fuels as raw materials which resulted in a significant amount of CO2 emission. Going forward, syngas need to be produced in carbon neutral or by negative carbon production methods. While blue syngas can be produced using conventional methods for fossil fuels followed by a carbon capture strategy, in the long term this strategy is still not sufficient to achieve our global warming goals and this strategy is also expensive. Green syngas uses renewable biomass, renewable solar and wind power, and CO2 utilization strategies. While significant work still needs to be done to make green syngas economically at a commercial scale, it is only a syngas type that is sustainable for a long period. The book examines this important Chemical energy vector.

Ammonia consists of 17.6 wt% hydrogen, showing that ammonia is an indirect hydrogen storage compound. Ammonia's energy density is 4.32 kWh/liter, which is similar to methanol (CH_3OH), and approximately double that of liquid hydrogen. Liquefying hydrogen is more difficult when compared to ammonia since ammonia liquefies at −33.4°C and at atmospheric pressure: Hydrogen has to be liquefied by chilling to temperatures lower than −253°C. One of the main challenges of utilizing hydrogen as an energy carrier is the difficulty of transporting and storing it without dissipating, and therefore being unavailable for its intended end use. Hydrogen also has some safety issues during transportation and storage and its low density causes difficulty in handling. The density of anhydrous ammonia, on the other hand, is 10.1 MJ/L which is approximately 1.5 times higher than of liquid hydrogen. From a safety point of view, ammonia gas is almost the same as air, so in case of leakage ammonia rapidly dissipates into the atmosphere. However, unlike hydrogen, ammonia is not typically explosive. It is a hazardous chemical and it must be handled with care, due to its causticity and toxicity. All these factors make ammonia a practical energy vector for hydrogen. Ammonia is also of crucial importance to the growth of agriculture worldwide and consequently, for maintaining the growth of the human population. Ammonia can also be utilized in the production of polyimides, nitric acid, nylon, pharmaceuticals, explosive materials, refrigerants, dyes, cleaning solutions, and other industrial chemicals. Thus ammonia is a significant chemical energy vector and the development of an ammonia economy along with hydrogen economy is essential.

The use of methanol as a fuel, either by itself, in a blend with gasoline, for the production of biodiesel, or in the form of methyl *tert*-butyl ether (MTBE) and dimethyl ether (DME), has also grown rapidly since the mid-2000s. Together these fuel uses now represent about 31% of methanol consumption. MTBE has been used as an oxygenated anti-knock fuel additive in gasoline since the 1980s. Biodiesel can be obtained by reacting methanol with fats and oils. However, the direct use of methanol as a fuel has seen the largest growth; from less than 1% in 2000, the share of methanol consumption for that purpose has now increased to more than 14%. Due to its high octane rating, methanol can be used as an additive or substitute for gasoline in internal combustion engines (ICEs). Methanol can also be used in modified diesel engines and advanced hybrid and fuel-cell vehicles. An added benefit of using methanol is that the same fuel can power both conventional ICE vehicles and FCVs, leading to a seamless transition to these more advanced powertrains. The Research Association for Combustion Engines (FVV) has conducted a study of e-fuels' potential in Germany. It determined that the e-fuels offering the lowest mobility cost for cars and trucks were e-methanol, e-DME, and e-methane. For aviation purposes, methanol could be converted to kerosene-type aviation fuels using a process similar to the methanol-to-gasoline (MTG) process. In the future, along with the hydrogen economy, the methanol economy will rapidly grow as its applications as a chemical intermediate and hydrogen donor for fuel cells expand. Renewable green methanol is the most sustainable chemical energy vector for the long term.

Finally, biomass is an important source of renewable biofuels to improve environmental conditions. Biofuels are derived from biological materials such as food crops, crop residues, forest residues, animal wastes, and landfills. Four biofuels of vital importance for the future are biogas, bio-ethanol, and bio-diesel or green and renewable diesel oil and sustainable aviation fuel. Biofuels their very nature, are renewable over less than one year for those based on crops, crop residues, and animal wastes or about 35 years for those based on forest residues. Once again, the development of green biofuels is very important for the full development of the hydrogen economy. The replacement of petroleum-based methane, ethanol, diesel, and jet fuel by biofuels is essential to develop carbon carbon-neutral energy industry.

This book describes in detail the roles of these five chemical energy vectors; hydrogen, syngas, ammonia, methanol, and biofuels which will be most sustainable in future hydrogen economy and carbon neutral energy industry. While in transition, different colors of energy vectors will play important roles, in the long term green energy vectors will be the most sustainable. The book will be very useful for undergraduate and graduate studies on the energy industry and for all researchers in academia, industry, and government organizations who are interested in the hydrogen economy and the future of the carbon-neutral energy industry.

CHAPTER 1

SUSTAINABLE SYNFUELS IN CARBON NEUTRAL ENERGY INDUSTRY: ELEMENTS OF HYDROGEN ECONOMY

1.1 Introduction – Why hydrogen economy?

It is now well accepted that the removal of carbon from the environment is essential for the protection from global warming and the resulting harmful climate changes. In the past, the energy industry was heavily dependent on non-renewable fossil fuels. The use of fossil fuels for power, heating, and cooling needs and the production of chemicals and fuels have resulted in unacceptable levels of carbon emission in the environment. Going forward, energy will become more and more dependent on electricity and hydrogen and its derivatives. Along with their use for power, the use of fossil fuels for chemicals and fuels also needs to be reduced. For all practical purposes, we are moving into the electrical and hydrogen economy. Electricity will dominate the future because its use is environment friendly and it will be needed due to the enormous growth in digitalization, automation, the internet of things, and personal electronics. The use of renewable sources for electricity generation must increase. In the future, power, chemicals, and fuels need to be generated from non-fossil fuel sources. This will inevitably result in the development of renewable sources of power and the hydrogen economy. Renewable energy sources including solar, wind, hydro, geothermal, ocean thermal energy conversion (OTEC), and biomass are the leading candidates to replace fossil fuels [**Ishaq and Dincer, 2020,275-307**]. **Figure 1.1** depicts the current proportion of the world's energy supply. A massive 35% of the world's energy supply comes from coal, followed by a 23% share from gas, 16% from hydropower and 10% from nuclear. Renewable energy sources contribute around 13%, which includes 7% from wind energy, 4% from solar, around 2% from Hydrogen, and the rest from biomass and biogas. Annual CO_2 emissions from different types of fuels are shown in **Figure 1.2**.

Dash et al. (Dash et al., 2023, 1141-1152) point out that coal, oil, and gas combustion result in 40%,32%, and 21% respectively global emissions followed by 4% from the cement industry. Presently the contribution of Hydrogen in the energy sector is negligible and when hydrogen is produced from renewable energy sources, the net CO_2 emission is much less compared to other fuels.

Hydrogen can replace fossil fuels as a fuel as well as an energy transporter and a storage medium. In order to attain net-zero CO_2 emissions by 2050, it would be crucial to decarbonize the main power, chemical, material, and food industries [**Nieto, 2022,170-177**]. Hydrogen is a carbon-free fuel solution and it is a raw material for many chemical, material, and food industries. The infrastructure for fuel storage and transportation that is now used for other chemical fuels can be a potential option for hydrogen storage and delivery. As shown in this book, several derivatives of hydrogen can also play important roles as chemical energy vectors to offset certain thermodynamic and chemical deficiencies of pure hydrogen as a source of chemicals, fuels, and energy carriers.

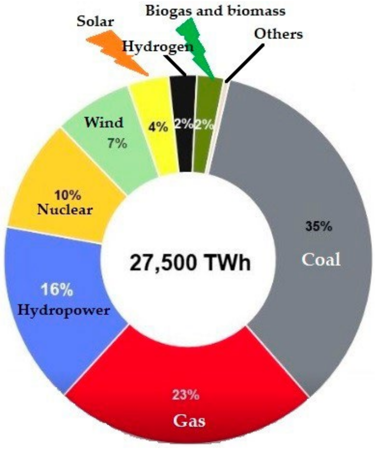

Figure 1.1 Global share of energy sources 2021 [Dash et al., 2023, 1141-1152].

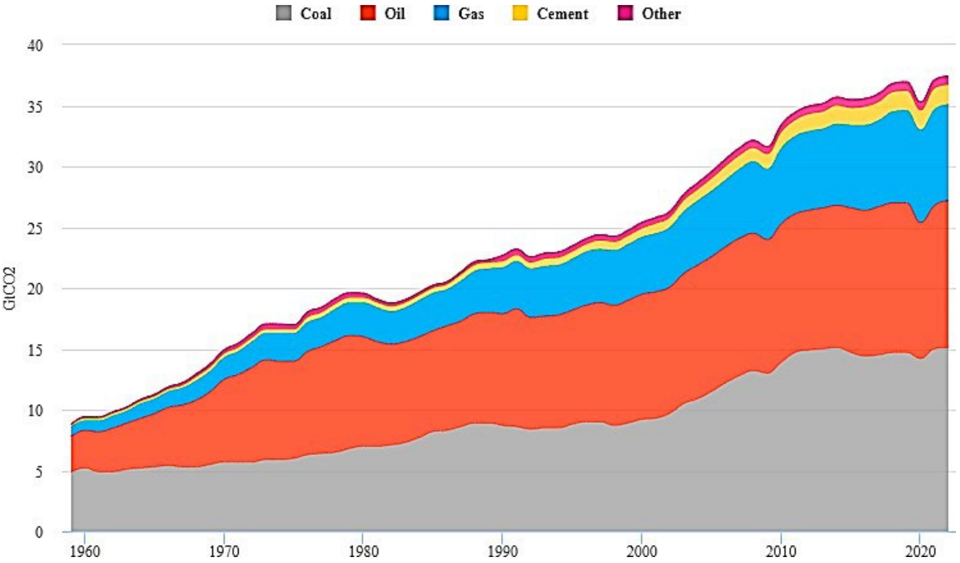

Figure 1.2. Annual CO2 emissions from different types of fuels (Dash et al., 2023, 1141-1152).

A full development of a hydrogen economy must satisfy certain conditions in its entire value chain. In this economy, green hydrogen must be produced using renewable sources like solar, wind, geothermal, water, and biomass. Such power-to-gas technology must use water, CO2, or biomass as raw materials. The storage of power, particularly for long-distance transport requires fuels. These fuel needs should be satisfied by green hydrogen or more favorable hydrogen-based green syngas, green ammonia, methanol, or biofuels. The chemicals and fuels should be produced by hydrogen or more favorably hydrogen-based green syngas or methanol which are very good chemical intermediates. The fuels for internal combustion engines, gas turbines, jet engines, and fuel cells should be provided by green hydrogen or green syngas, green ammonia, green methanol, or green biofuels. Finally, if hydrogen is used in a mixture with methane, efforts must be made to capture CO2 generated by the process.

The theme of the present book is that the full impact of the hydrogen economy on power, chemicals, fuels, and food industries is best achieved by simultaneously developing the four other most important chemical energy vectors besides hydrogen. Together, hydrogen, syngas, ammonia, methanol, and biofuels provide multiple functions for chemicals, chemical intermediates, fuels for energy storage and long-distance transport, and additional safety. These are called sustainable chemical energy vectors or sustainable synfuels because they are useful for both energy and chemicals and fuels that are sustainable over the long haul. Furthermore, as long as these vectors are not generated from fossil fuels, their production, storage, and use can be carbon neutral. The book will elucidate the versatility of these five energy vectors and examine how they can be produced renewably without the use of fossil fuels, and how they can be used for chemical and fuel needs in a sustainable manner. The book will demonstrate in detail that renewable and sustainable blue and green fuel generations and their use in totality will underpin the full-scale development of the hydrogen economy.

In the hydrogen economy, hydrogen or its derivatives must be able to provide sustainable fuels and chemicals. Hydrogen is a carbon-free source of fuel and carries some important fuel properties. **Table 1.1** obtained from the study of Dash et al. (Dash et al., 2023, 1141-1152), lists comparisons of the main technical parameters of hydrogen with other fuels like methane and diesel oil. Among all other fuels, whether they be liquids or gases, hydrogen delivers the fastest burning rate. The hydrogen fuel cells provide a high-performance indication in terms of efficiency since they are not limited by the Carnot cycle's thermal efficiency restrictions. In order to support hydrogen-powered fuel cells and fuel cell-based hybrid automobiles, it is anticipated that a significant quantity of H_2 refueling stations will be built in the near future. Some of the key benefits of hydrogen include effective conversion of energy; production through water splitting with no carbon emissions; synthesis of various intermediate fuels, including syngas, methanol, biofuels, and ammonia, followed by various chemical reactions producing a large number of chemicals and other synfuels; storage availability; ability to use in existing infrastructure for long-distance transportation; and a high LHV in comparison to other fuels.

Table 1.1 The main technical characteristics of hydrogen vs. other fuels [Dash et al., 2023, 1141-1152].

Parameter	**Hydrogen**	**Diesel**	**Methane**
Density at STP (kg/m3)	0.089	830.0	0.720
Volumetric energy at STP (MJ/m3)	1.07 × 10	3.5 × 104	3.3 × 10
Net Lower Heating value (MJ/kg)	119.9	42.5	45.8
Boiling point (K)	20.0	453–633	111.0
Auto-ignition temperature (K)	853	~523	813
Minimum ignition energy in air at 1 bar stoichiometry (mJ)	&0.020	0.240	0.290
Stoichiometry air/fuel mass ratio	34.4	14.5	17.2
Quenching distance at NTP (mm)	0.64	-	2.1
Laminar flame speed in air at NTP (m/s)	1.85	0.37–0.43	0.38
Diffusion coefficient in air at STP (m2/s)	85 × 10−7	-	19 × 10−7
Flammability limits in air (% vol)	4–76	0.6–5.5	5.3–15
Adiabatic flame temperature at NTP (K)	2480	~2300	2214

Hydrogen is an energy carrier with a wide range of properties to be used as fuel, as raw material, or as an interface between electricity and chemical energy through the power-to-gas process. It can be used as a storage medium to absorb the renewables fluctuations and/or as feedstock for emission-free synthetic natural gas production through methanation reaction. Its high content of energy per mass (higher heating value 142 MJ/kg), is around three times larger than natural gas (53.6 MJ/kg), diesel (45.4MJ/kg), and gasoline (46.4MJ/kg). Additionally, its capability to enable the decarbonization of some chemical processes and the transport sector makes hydrogen a key energy carrier to resolve the current energy and environmental challenges (Dash et al., 2023, 1141-1152;4,41). It has been known that renewable energy sources like wind and solar are intermittent and require storage for their dispatchable use. Hydrogen, which is considered an alternative energy carrier, is proposed to play a significant role in the future energy industry because it can be stored and transported and has a high calorific combustion value, making it suitable to replace fossil fuels (Saxena and Kumar, 2008, 1909-1927). As shown in this chapter, its eco-friendly production process supports its sustainability and eco-friendly character (Joshi and Dincer, 2010, 4901-4908). Moreover, hydrogen can be directly applied to fuel cells to produce electricity without any toxic emissions but with an energy yield of about 122 KJ/g, which is 2.75 times greater than hydrocarbon fuels (Fan and Chan, 2021, 8421-8446).

Some now argue that a true decarbonized economy cannot be achieved without the use of hydrogen for power, chemicals, and fuels. Like the U.S., the European Commission is determined to make Europe deliver on its ambitious climate promise to achieve carbon neutrality by 2050; and point out that commitment to green hydrogen technology and its versatile applications in the fuel, chemical, and food sectors along with its use in industry to buildings to transportation will clear the path towards this goal (Saxena and Kumar, 2008, 1909-1927;5-14; Joshi and Dincer, 2010, 4901-4908; Fan and Chan, 2021, 8421-8446; Zhnag et al., 2016, 14535-14552; Shah et al., 2022, 135001-135009; Nnabuife et al., 2022, 100042-100056; Osman et al,2022, 153-188; Hematpur et al., 2023, 111-131; Salahu et al., 2022, 461-499; Haider et al., 2021, 1671-1681). Figure 1.3 shows a generic scheme of hydrogen's value chain, hinting that to frame the implementation of this strategy, it is important to first define the configurations considered to be priorities in the hydrogen value chain—from production to final consumption. While natural gas is the primary source of hydrogen production, ammonia manufacturing is the most hydrogen-consuming industry. Furthermore, hydrogen transportation from the production site to the consumption site is a vital process in the hydrogen production economies because it can increase production costs, influencing its affordability. Hydrogen storage is considered an urgent and challenging stage because it helps develop safe, reliable, efficient, and adequate storage mechanisms (Zhnag et al., 2016, 14535-14552). The successful hydrogen economy will also need to have a path to transport hydrogen across land and sea.

As shown in Figure 1.3, IRENA (IRENA, 2019) points out that there are three stages for the hydrogen value chain. The first stage of the hydrogen value chain consists of its production, with different pathways, processes, and associated technologies. Depending on the required scale, large-scale (centralized) production is distinguished from small-scale (decentralized) production—ideally, close to the place of consumption. Currently, hydrogen is generated in the order 48%,30%,18%, and 4% from natural gas, oil, coal, and electrolysis of water respectively. This is the most important stage for the green hydrogen economy. In order to avoid carbon emission during hydrogen production that presently occurs, going forward, the production of green hydrogen will require the use of renewable power and the dominant use of both large and small-scale electrolysis processes. The use of CO2 to produce green hydrogen will also be the dominant subject of investigation.

1.2 Hydrogen value chain

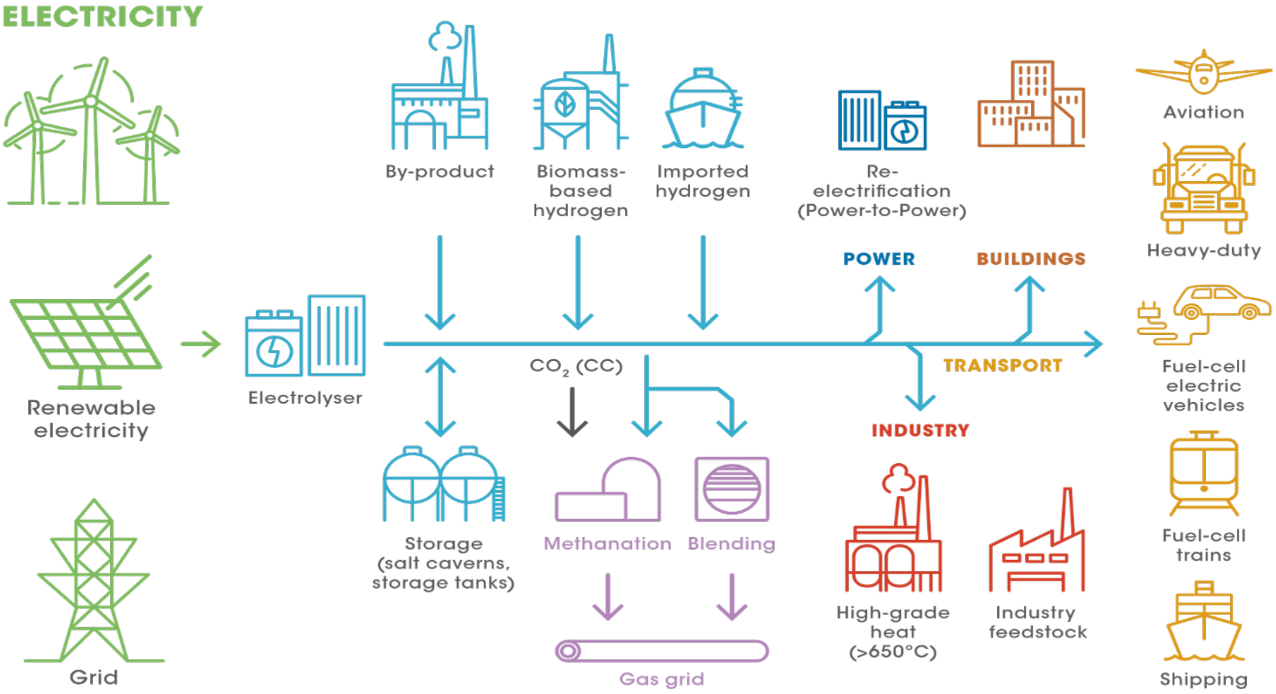

Figure 1.3. Concept of $P2H_2$ and the end-use applications of hydrogen (IRENA, 2019)

As mentioned above, in order to produce green hydrogen, the power required for the electrolysis must come from renewable sources like solar (PV or CSP), wind, geothermal, hydro, OTEC, etc. Recent reviews of Shah et al. (Shah et al., 2022, 135001-135009) and Mahmoud etal. (Mahmoud etal. , 2021, 100854-100869) examined the use of geopower for electrolysis. They examined characteristics, such as *water electrolysis* temperature, working fluid, *geothermal fluid* temperature, & power cycle type. The studies compared various types of *geothermal power* plants, such as flash, flash-binary, binary, and *ORC* cycles. The research also included studies on hydrogen production rates and costs, energetic costs, and the quantity of power produced using geopower. Mahmoud et al. (Mahmoud etal. , 2021, 100854-100869) found that hydrogen production rates vary from 5,439 kg/h to 13958 kg/h. *Multigeneration* systems showed great potential to enhance the overall system's efficiency, leading to reduced production costs. The integration of another energy source was found to be interesting in geothermal-driven hydrogen production systems. This would promote the adoption of a multigeneration system as well as increase the geothermal fluid's temperature before entering the power cycle. The use of excess hydropower for electrolysis in order to improve the efficiency of hydropower has also been investigated in the literature. The produced hydrogen can also be used for fuel cells to generate additional power. Tarnay (Tarnay, 1985) evaluated hydrogen production by hydropower plants. Hydro-Québec and thyssenkrupp have created systems to operate large-scale electrolysis using hydropower. As shown later in this book, the use of OTEC to supply energy for electrolysis is also being investigated.

Since solar and wind power are available everywhere in the world, generally excess power generated from solar and wind sources is used for electrolysis. Although PV panels and wind turbines are directly coupled with electrolyzers, CSP is first associated with a power cycle for electricity production before connecting them to electrolyzers, which requires an AC/DC or DC/DC converter for electrolyzer load adjustments. Hydrogen generated by electrolysis can also be used to generate power during the night using fuel cells. Nasser et al. (Nassar et al., 2022, 86994-87018) examined the PV/H2, multigeneration PV/H2 system, Wind/H2 system, CSP/H2 systems, and hybrid wind/PV/CSP/H2 system for the use of renewable energy for electrolysis. Their overall system examined in this study is graphically illustrated in Figure 1.4. As shown by Nasser et al. (Nassar et al., 2022, 86994-87018), in a PV/H_2 system, PV panels are linked to an electrolyzer through a power-conditioning unit containing a maximum power point tracking (MPPT) system and a DC/DC converter. This unit is applied to maximize the output from panels and adjust the electrolyzer input power (Aydin et al., 2021, 111793-11808; Nassar et al., 2022,115870-115888; Nassar et al., 2022, 102195-102209). The excess electricity from PV systems is stored in the battery. PV/H2 system requires low maintenance due to the absence of moving parts and it also generates DC electricity output. On the other hand, in the CSP/H_2 system, solar radiation heat is divided into two portions: the first is used in power cycles (e.g., organic Rankine cycle (ORC)) to generate electricity that drives the electrolyzer, and the second converts water to steam by employing SOE, as shown in Fig. 1.4 (Chadegani et al., 2018, 20-32). Through the use of electricity and heat, the CSP/H2 system can be continuously operated. Joshi et al. (Joshi et al., 2011, 11246-11257) compared PV/H_2 and CSP/H_2 under the same conditions and showed that the CSP/H_2 system performed better than PV/H_2. The wind/hydrogen production (wind/H_2) system is more like a PV/H_2 system but needs an AC/DC converter to drive the electrolyzer. This system suffers from unpredictability. With all these pluses and minuses of different systems, it is clear that a hybrid system illustrated in Figure 1.4, provides the most sustainable option to enhance a system's efficiency and provide a multi-generation cycle (Nassar et al., 2022, 86994-87018).

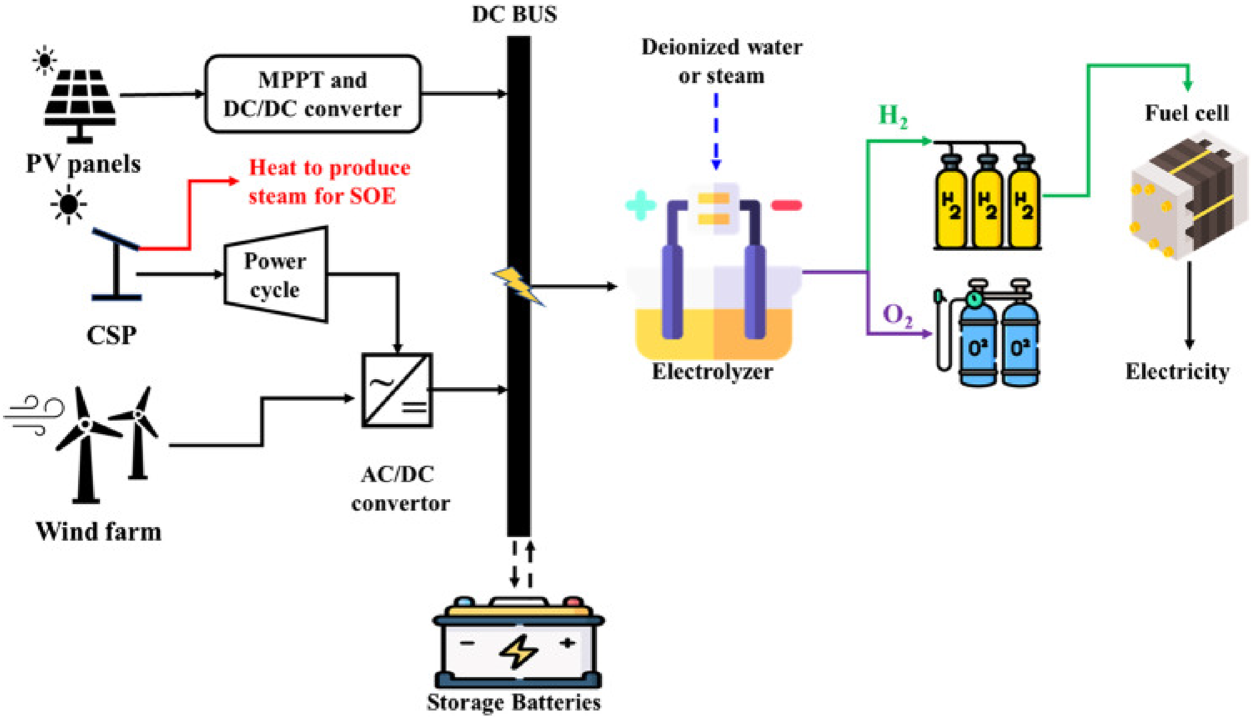

Figure 1.4. The schematic diagram for solar/wind hydrogen production systems (Nassar et al., 2022, 86994-87018)

The hybrid system proposed by Nassar et al. (Nassar et al., 2022, 86994-87018, Nassar et al., 2022,115870-115888; Nassar et al., 2022, 102195-102209) (Figure 1.4) reduces cost and offers continuity in power production. Additionally, it allows selling hydrogen at 10 €/kg which is economically viable in areas with high wind speed. The hybrid can be created by combining PV/H_2 and wind/H_2 systems (Nassar et al., 2022, 86994-87018; Akyuz et al., 2012, 16623-1663022) and they provide hydrogen production of 30.4 kg between April and July. The hydrogen production from the hybrid system is more than wind/H_2 and PV/H_2 systems by 26.2% and 127%, respectively (Nassar et al., 2022, 86994-87018; Khalilnejad and Riahy, 2014, 398-406). Cai et al. (Cai et al., 2020, 106-117) showed that the thermal efficiency of a combination of wind farms with CPVT is better than wind farms with CSP. Because of the higher power input in the electrolyzer and an increase in the water temperature by solar energy before entering the electrolyzer (Huang et al., 2016, 8514-8524), the hybrid system increases hydrogen production efficiency. The major cost of hydrogen production is the cost of electricity to electrolyzers which depends on the lifetime, land cost, and construction period for electricity production. The addition of a battery system reduces the interruptions in the process which results in an increase in working hours, efficiency, and lifetime (Ursua et al., 2016, 12852-12861). The hybrid system's utilization factor is higher than the single system (Papadopoulos et al., 2018, 16468-16478) and it can provide electricity for houses (Devrim and BIlir, 2016, 759-766), hydrogen for electric vehicles (Bernal-Agustín and Dufo-López, 2010, 747-758; Rezaei et al., 2019, 539-550; van der Roest et al., 2020, 114024-114038), hydrogen for urea and ammonia production (Nassar et al., 2022, 86994-87018; Nassar et al., 2022,115870-115888; Nassar et al., 2022, 102195-102209; Armijo and Philbert, 2020, 1541-1558; Ishaq et al., 2021, 4749-4760) and distilled water to the electrolyzer by powering the reverse osmosis system.

The hybrid system can also be used for space cooling, heating, and desalination(Sezer et al., 2019, 3263-3283). Wang et al. (Wang et al., 2021, 2594-2604) showed that the power can be generated from the heart dissipated from a fuel cell. The study (Nassar et al., 2022, 86994-87018) indicates that LCOE is higher for renewable sources compared to coal and nuclear. LCOH depends on electricity cost (Nassar et al., 2022, 86994-87018, Nassar et al., 2022,115870-115888; Nassar et al., 2022, 102195-102209) and the production methods (El-Emam and Ozcan, 2019, 593-609). Solar and wind energy are more expensive than conventional methods. LCOH for wind is lower than that for solar and it also depends on the nature of the electrolyzer (Nassar et al., 2022, 86994-87018, Olateju et al., 2014, 48-56; Greiner et al., 2007, 1500-1507; Mastropasqua et al., 2020, 114392-114403). Finally, the studies by Nasser et al. (Nassar et al., 2022, 86994-87018, Nassar et al., 2022,115870-115888; Nassar et al., 2022, 102195-102209) indicate that green hydrogen production is expensive and may remain so without government subsidy and policy action (Agaton et al., 2022, 17859-17870).

The second stage in Figure 1.3, starts with storage and ends with delivery for final use. Depending on the choices made, this stage includes underground gas storage, liquefaction, compression, storage and distribution in gas networks, road and maritime transport, or refueling. All of these sub-processes have their own risks and safety concerns that can be raised due to the operation at very low temperatures or very high pressures requiring tanks with high thickness and/or heavier insulation. Since the thermodynamic properties of hydrogen are not the most conducive for storage and long-distance transport due to leakage and explosion safety considerations, the use of other chemicals such as ammonia, methanol, or diesel oil is often considered. Section 1.8 evaluates in detail various storage and transport technologies for hydrogen.

Finally, in the third stage, the hydrogen value chain addresses the main end-use applications in the mobility/transport and industrial sectors. In residential and industrial stationary applications, mixtures of hydrogen and natural gas can be applied to generate heat and electricity. The end-user must consider in totality how hydrogen is going to be used as an energy vector. Currently, hydrogen use is 51%, 31%,10%, and 8% for ammonia, methanol, oil refining, and other uses respectively. The complete details of the end use of hydrogen are given in section 1.9.

1.3 Hydrogen as energy vector

It is now well-accepted that besides electricity, hydrogen is the most significant energy vector for the future. In addition to a carbon-free source of energy, hydrogen also plays an important role in the changes occurring in the energy supply system (Guilbert and Vitale,2021, 881-909). Currently, the power system is dominated by a centralized utility-based network system. Large-scale power productions are encouraged to take advantage of economies of scale. Going forward, however, distributed energy systems (DES) are becoming more important. DES is based on the idea that they replace or complement the large-scale and conventional centralized generation plants, with smaller units located close to energy consumers [Guilbert and Vitale,2021, 881-909; Fonseca et al., 2018, 510307e371]. This concept suggests a shift in the paradigm of energy framework, and appears as an alternative to face the energy and environmental challenges of the future; e.g. providing electricity to isolated communities, and reducing CO2 emissions in both static and mobile industries. Besides offering more flexibility in generation, and reducing inefficiencies in delivering and vulnerability of the system, DES can provide a reliable pathway for energy transition from the technological, economic, environmental, and social point of view. One of the key aspects of DES lies in the inclusion of multi-generation technologies and the use of renewable sources. Hence, by easing the integration of renewables through a flexible transformation system, DES allows to take advantage of the synergies among different sources and energy carriers while responding to electricity, heating, cooling, fuel, and even water demands [Guilbert and Vitale,2021, 881-909; Fonseca et al., 2018, 510307e371].

Guilbert and Vitale (Guilbert and Vitale,2021, 881-909) and Fonseca et al. (Fonseca et al., 2018, 510307e371) point out that among energy carriers, hydrogen has emerged as a friendly solution for climate change, air pollution, and energy security. Although hydrogen is the most abundant element on earth, it can only be found as a compound in water, fossil fuels, biomass, etc. [Guilbert and Vitale,2021, 881-909; Fonseca et al., 2018, 510307e371]. Hydrogen as an energy carrier and raw material has a wide range of applications that include fuel (e.g. transportation, power units), chemical industry (e.g. oil refining, fertilizers production), and energy storage and transport. When hydrogen is employed to store energy, it offers the possibility to be an interface among electricity, chemical, and heat energy networks through the so-called power-to-gas process [Guilbert and Vitale,2021, 881-909; Fonseca et al., 2018, 510307e371]. The use of hydrogen as storage for intermittent power supply, raw material for distributed fuel cells, and its direct use as fuel to generate only steam and heat makes it a very valuable energy vector. In order for a proper assessment of hydrogen in a multi-generation system, DES requires an integrated approach with economic, environmental, and socio/political dimensions. In order to satisfy the use of hydrogen in its totality from a global perspective, its application should be designed, selected, and operated with proper modeling and optimization (Guilbert and Vitale,2021, 881-909; Fonseca et al., 2018, 510307e371). In recent years, the focus has been to develop power plants located close to end-users and designed according to local resources and demands, in addition to renewable sources deployment. These issues have been addressed under the DES concept, which involves both the placement of generation plants (decentralized generation) and the integration of different energy sources.

In DES, the distributed generation can offer technical, economic, and social advantages and electricity demand can be classified based on the level of distribution; peak demand of less than 20 kW for households, between 20 and 80 kW for remote villages, and between 90 to 150 kW for urban area. According to the increasing interest in DES, a diversity of aggregation concepts and approaches has emerged in the scientific community. These include the concepts of energy hubs, micro and nano grids, multi-energy systems, polygeneration, and hybrid energy systems. All of these concepts can be facilitated through the hydrogen economy. Unfortunately, hydrogen has some deficiencies in its use not only as an energy carrier but also for chemicals and the food industry. These deficiencies can be overcome by the simultaneous development of several hydrogen-based chemical energy vectors such as syngas, ammonia, methanol, and biofuels. This book addresses the development of these sustainable chemical energy vectors. The premise of this book is that the hydrogen economy cannot be fully developed without simultaneous developments of syngas, ammonia, methanol, and biofuel economy. Together these chemical energy vectors will best serve the mission of decarbonization of energy, chemical, and food industries (Guilbert and Vitale,2021, 881-909; Fonseca et al., 2018, 510307e371).

1.4 Types and Colors of Hydrogen

Hydrogen can be produced from a number of different sources and by different technologies. The idea of color has been developed as a result of the use of important sources in the generation of hydrogen. Grey hydrogen is the result of the applications of steam reforming, gasification, partial oxidation, auto thermal reforming, etc. to various fossil fuels without capturing CO2 emission. A by-product of other chemical processes also produces more than 40% of grey hydrogen [Dash et al., 2023, 1141-1152; Kannah et al., 2021, 124175-124188]. The reforming of natural gas is a major source of grey hydrogen production. Another common technique for producing grey hydrogen is coal gasification. The syngas produced from gasification is then cooled rapidly and the recovered heat is utilized for a variety of things including electricity generation, hot water production, and space heating. The water gas shift reaction follows the syngas cooling unit, which converts CO into CO_2. If this CO2 is emitted in air the hydrogen is grey hydrogen. However, if CO2 is captured using a pressure swing adsorption unit then it is called blue hydrogen. White hydrogen has also been unofficially coined by the North American Council for Freight Efficiency [Roeth, 2021]. Grey hydrogen is mostly used in the petrochemical industry and in the production of ammonia [Wang, 2021, 38612-38635] and it is estimated to emit 830 Mt of CO_2 yearly [Woody and Carlson, ,2020].

Purple hydrogen is produced using heat or power from nuclear energy. The heat from nuclear energy is used to create steam, which is then used in turbines to create electricity [IRENA, 2022; Calise et al., , 2019]. Nuclear power plants do not emit any greenhouse gases. The fission process in the nuclear reactor serves as the heat source for the thermal energy in a nuclear power plant [Dash et al., 2023, 1141-1152; Pinsky et al., 2020, 103317-103329]. This thermal energy turns a turbine to generate electricity, which may then be used to power fuel cells to create hydrogen [Dash et al., 2023, 1141-1152; Milewski et al., 2021, 35765-35776]. Thermal energy and electricity can also be used for steam reforming of natural gas, water electrolysis, or thermochemical water splitting cycles.

Hydrocarbons split to generate turquoise hydrogen. This may be accomplished using a variety of methods. Most researched and likely to be commercialized is the plasma process for producing carbon black and hydrogen. Other techniques include cold plasma, methane catalytic conversion, and molten metal pyrolysis via thermal splitting [Corey, 2021]. The most widely used hydrocarbon is natural gas which provides both process energy and electricity. Methane splitting potentially requires 38 kJ/mol H_2, while water electrolysis requires 285 kJ/mol H_2, and steam-methane reforming requires 252 kJ/mol H_2. Methane splitting requires high temperatures and is accompanied by heat losses [Schneidert et al., 2020, 150-158].

Processes involving grey hydrogen can produce blue hydrogen if they are accompanied by carbon capture technology to reduce CO2 emission [Dickel, 2020; Mari et al., 2016, 4969-4992]. Current conventional hydrogen production facilities integrate carbon capture and storage (CCS) or carbon capture and utilization (CCU) systems to collect the discharged CO_2 emissions. Blue hydrogen can also be produced using renewable biomass sources. The blue hydrogen production method is depicted in **Figure 1.5.**

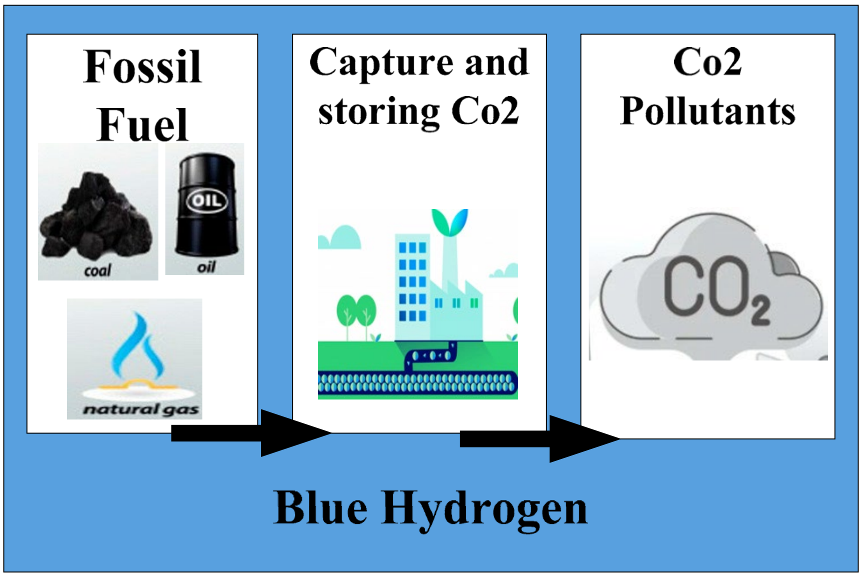

Figure 1.5. Schematic of Blue hydrogen production (Dash et al., 2023, 1141-1152).

Green hydrogen is produced when water is electrolyzed with electricity produced by renewable energy sources or low-carbon power sources. Currently, electrolysis is the most established commercially accessible process for producing hydrogen from water. Water electrolysis is the process of dissociating water into its component elements, hydrogen, and oxygen, using an electric current. Positive ions (H+) are drawn to the cathode by the electric potential, whereas negative ions (OH-) are drawn to the anode. Alkaline water electrolysis (AEL), proton exchange membrane (PEM) water electrolysis, solid oxide water electrolysis (SOE), and alkaline anion exchange membrane (AEM) water electrolysis are some of the water electrolysis methods discussed in this chapter. Besides them, there are other modifications of conventional electrolysis such as hybrid electrolysis and photoelectrochemical dissociation of water also generate green hydrogen. Green hydrogen can also be produced by thermochemical processes such as gasification and reforming of biomass or thermochemical cycles for the splitting of water. Biochemical processes like dark and photo fermentation, and anaerobic digestion applied to biomass also produce green hydrogen. CO2 generated from these processes must be captured and stored or utilized. All of these processes are discussed in detail in the remainder of the chapter. Green hydrogen is the only sustainable form for the long term.

1.5 Thermochemical methods for hydrogen production

Hydrogen can be produced from various energy sources by adopting a range of production methods. Water electrolysis using renewable or nuclear electricity, steam reforming of natural gas, biomass gasification, biochemical processes such as dark fermentation and anaerobic digestion, and solar energy-driven thermal splitting, photoelectric catalytic process, and solar PV power electrocatalytic process are some of the processes being pursued. The old coal gasification and subsequent reforming processes are being slowly wiped out due to their harmful effects on the environment. As shown earlier, these processes can be accompanied by carbon capture and storage technology to generate blue hydrogen. (Germscheidt et al., 2021, 2100093).

Nikolaidis and Poullikkas (Nikolaidis and Poullikkas, 2017, 597-611) evaluated 14 different hydrogen production processes including the ones involving conventional and renewable sources. The study indicates that gasification and pyrolysis processes of renewable materials like biomass have the largest potential to become large-scale processes for hydrogen production (Bičáková and Straka, 2012, 11563-11578; Sazali, 2020, 18753-18771). Dawood et al. (Dawood et al., 2020, 3847-3869) analyzed a novel hydrogen square model for the production, storage, safety, and utilization of hydrogen and proposed a hydrogen cleanness index to designate the color of hydrogen. Acar and Dincer (Acar and Dincer, 2019, 835-849) evaluated processes for hydrogen production, type of energy used, and storage methods and presented a comparative assessment of different processes. Several reviews (Kannah et al., 2021, 124175, Bičáková and Straka, 2012, 11563-11578; Versa et al., 2017, 2018-2033; Sazali, 2020, 18753-18771) have also evaluated techno-economic assessment of various hydrogen production methods which used renewable power sources.

So far, a lion's share of grey or blue hydrogen has been produced by gasification or reforming technologies using natural gas or coal as feedstock. In fact, currently, hydrogen is produced from natural gas, oil, coal, and electrolysis is 48%,30%, 18%, and 4% respectively. In recent years, biomass is also increasingly used as feedstock in order to reduce net CO2 emissions to the environment. Both gasification and steam reforming technologies are mature and are commercially practiced for a long period. Going forward, these technologies can reduce CO2 emission by either capturing or utilizing CO2 emission or using biomass as feedstock with or without carbon capture technologies. Here we briefly describe these technologies with a particular emphasis on the use of biomass as feedstock.

Hydrogen can also be produced by thermochemical cycles using solar energy as a heat source. Numerous cycles (two, three, or multi-steps) with different metal oxide oxygen carriers have been proposed. Hydrogen can also be produced using photocatalysis in a number of different ways. Here we briefly review all of these methods.

1.5.1 Gasification

Gasification is a thermo-chemical conversion process for solid or liquid carbonaceous materials (coal, oil, or biomass) to mainly produce syngas consisting of hydrogen and carbon monoxide. However, depending on the feedstock and operating conditions, CH4, H2S, CO2, and NH3 can also be produced [Rozzi et al., 2020, 420-433]. This technology is very mature and in the past extensively used for coal. Due to its significant impact on the environment, going forward coal and oil will be replaced by biomass. While discussing its basic features, in this chapter we will mainly focus on the use of this technology for biomass.

Unlike coal, since biomass is very non-homogeneous, containing different species and impurities, the product gas coming out of biomass gasification may have to be treated in accordance with the nature of the feedstock. Gasification of biomass is a multi-step process that first involves a feed preparation step which may include drying, torrefaction, grinding, pelletization, etc. This step is then followed by pyrolysis in the absence of oxygen in order to release volatile compounds (mainly CH4, CO, and H2). In the next step, an oxygen-controlled environment is supplied to the system for the combustion of the volatile matter, which helps to increase the process temperature and provides the medium for the subsequent operation. Finally, the gasification ends with the reactions between the biochar and a gas phase mainly composed of CO2, H2O, and O2 under temperatures of 800-1300°C [Zhang et al., 2020, 13438-13455; Alves et al, 2023, 3505-3540]. Following gasification, depending on the end-use of the syngas produced, the product gas is further subjected to water-gas shift reaction and/or purification processes to employ it as fuel, or raw material for methanol or synthetic natural gas production (methanation) [Zhang et al., 2020, 13438-13455; Alves et al, 2023, 3505-3540]. This process is more complex than one for coal, which is more homogeneous than biomass; however, the basic steps still apply. A typical biomass gasification process, as depicted by Alptekin and Celiktas (Alptekin and Celiktas,2022,24918-24941) is illustrated in Figure 1.6.

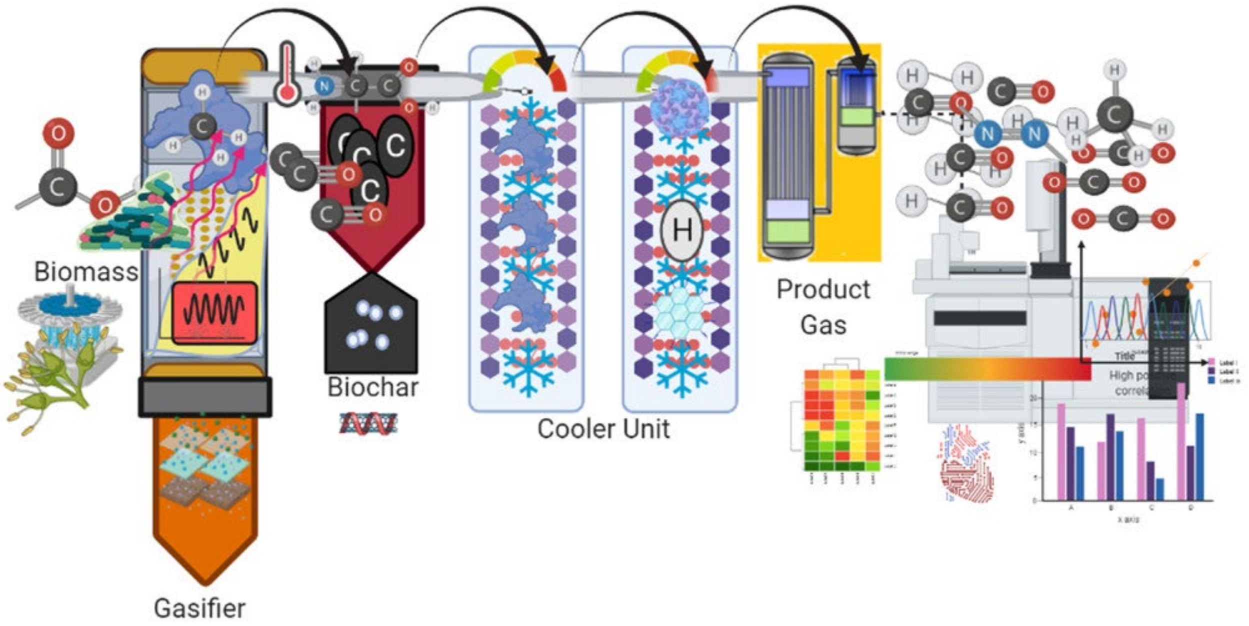

Figure 1.6: A typical biomass gasification process (Alptekin, and Celiktas, 2022, 24918-24941)

In general, gasifiers can be classified according to a wide variety of characteristics such as nature of feedstock, bed temperature and type, pressure, oxidant flow through the equipment, residence time, and the nature of ash formations [Rozzi et al., 2020, 420-433; Ursua et al., 2011, 410-426]. The most common types of gasifiers used are entrained-flow, fixed-bed, and fluidized-bed with possible upflow downflow, and counter-current flow configurations. Currently, entrained-flow gasifiers are the most efficient alternative for coal and, have the smallest environmental impact and the largest production capacity, thus they represent the major part of the commercial market for centralized coal-based syngas plants [Zhang et al., 2020, 13438-13455; Alves et al, 2023, 3505-3540]. This technology is characterized by operating at high temperatures (1100-1500°C), which allows good conversions in short reaction times and avoids technical limitations in the feedstock type. Fluidized bed or circulating fluidized bed equipment offers a homogeneous temperature environment promoting heat and mass transfer between the reactants. The main advantages of these gasifiers are their easy scale-up and adaptation to changes in the feedstock, as well as better temperature control, whereas their drawbacks are related to the need for specific particle size and lower conversion with respect to other gasification options [Zhang et al., 2020, 13438-13455; Alves et al, 2023, 3505-3540]. For biomass gasification, fixed-bed reactors are commonly used and are divided into concurrent (downdraft) and counter-current (updraft) gasifiers. For small-scale and on-site applications, downdraft gasifiers are the preferred option due to their relatively easy design, fabrication, and operation, as well as their low tar content in the product [Ursua et al., 2011, 410-426; Lin et al., 2021, 569-580]. They, however, pose some challenges due to the channeling effect, and show limitations in obtaining good performances with feedstock moisture over 20% [Zhang et al., 2020, 13438-13455; Alves et al, 2023, 3505-3540].

Biomass has low energy density, and high oxygen content and contains a variety of materials such as human and animal waste, forest and agricultural products, municipal biowastes, etc. [Babu,2012,246-256; Goransson and Soderlind, 2011, 482-492; Molino et al., 2016, 10-25], and its gasification can produce hydrogen, along with other byproducts. As shown in Equation (1.1), glucose (a typical ingredient of biomass) gasification results in the production of carbon mono-/dioxide and hydrogen, at high temperatures, in the presence of oxygen and steam.

$$C_6H_{12}O_6 + O_2 + 2H_2O \rightarrow 2CO + 4CO_2 + 8H_2 \qquad (1.1)$$

Unlike coal, biomass contains more cellulosic carbon and glucose is an important component among others. The products of this reaction (namely producer gas) are then subjected to a water gas shift reaction to produce a mixture of hydrogen and carbon dioxide which is separated using membrane technology to recover pure green hydrogen.

The gasification of biomass is more complex than that of coal because of its varied properties, complex shape and size of different feedstock, and high oxygen content. As mentioned before, this requires a complex feed pretreatment process before biomass pyrolysis and gasification. Biomass does not gasify as easily as coal and requires both pyrolysis and gasification stages. The products of biomass gasification contain various impurities like sulfur, chlorine, nitrogen compounds, phosphorous, some heavy metals, and others and require rigorous purification before they can be used to recover hydrogen or for any other downstream operations. Once purified, hydrogen can be separated from CO_2 using membrane technology. In recent years more efforts have been made to gasify coal-biomass mixtures or biomass alone.

The subject of coal-biomass mixture gasification is treated in detail in my previous book (Shah, 2015). The main reason for mixture gasification is to reduce net CO2 emissions in the environment.

The gasification process can be further facilitated with the use of catalysts. Alptekin and Celiktas (Alptekin and Celiktas,2022,24918-24941) pointed out that catalysts can play a major role in biomass gasification. Their review indicates that alkali and alkaline earth metal catalysts, Ni-based catalysts, natural mineral catalysts, and waste byproducts are applied as catalyst precursors in biomass gasification. However, each of these catalysts has merit and demerits to be improved to enhance the process and syngas yield. Through STEEP analysis, the study concluded that academic studies on catalyst development and their commercial applications have not progressed simultaneously. Correspondingly, the STEEP analysis showed that more catalyst development, specifically for biomass gasification, is required and it needs to be simultaneously applied by industry. In order to achieve a greener and more sustainable future, the currently used catalysts must move toward being more stable, efficient, economical, and reusable and must contribute to less energy-intensive processes.

Hydrothermal gasification in the presence of water is another technique used to increase hydrogen production. Paida et al. (Paida et al., 2019, 25524-25541) showed that a two-step approach of hydrothermal gasification of carbohydrate-rich wastes and wastewaters is a promising route for H2 production and simultaneous clean-up of wastewater. In this study, experimental data and kinetic models were used to further develop the process on an industrial scale. Also, a preliminary process design was conducted in order to assess the market potential of the two-step process. For stabilization, two cases were considered: the use of excess vs. stoichiometric H2, and for gasification, the utilization of sequential reactors housing Pt and Ru catalysts was compared to a single reactor with Pt alone. A total of four options were conceptually designed and economically evaluated. Using state-of-the-art insights and process techniques and the current market scenario, a minimum H2 selling price of 3.4 $ kg1 was obtained. As depicted in Figure 1.7, Paida et al. (Paida et al., 2019, 25524-25541) successfully tested this two-step approach, using sucrose as a model carbohydrate [Shah et al., 2022, 135001]. For the treatment of aqueous carbohydrate streams derived from agricultural and food residues, stabilization prior to gasification would be useful. Such wastewater streams are present in several fruit processing industries, and have COD values up to 120 kg O2 m3 [Paida et al., 2019, 130-141].

In light of initial success, the use of hydrothermal gasification of biomass to generate energy and chemicals is being extensively investigated at the laboratory scale(Paida et al., 2019, 25524-25541; Elliott, 2008, 254-265). This appears to be a smart route because biomass already contains a significant amount of oxygen and the process alleviates the need for drying of biomass before gasification. While the process has been successfully used to produce hydrogen-rich gases, the coke produced from sugar is a major issue that results in a lower yield of gas production (Tanksale et al., 2007, 717-724). This issue is resolved by a pre-step of stabilization of sugar which makes it less prone to coke and char. Stabilization has been widely studied in the upgrading of pyrolysis oil in which lower temperatures were found to favor hydro-treating reactions over polymerization reactions [Mercader et al., 2011, 3160-3170]. A sensitivity study showed that the feedstock price, concentration, and quantity, played a crucial role in the selling price of H2. These variables were all correlated and were dependent on the industry from where the feedstock was obtained. Industrial wastewater streams rich in carbohydrate residues and associated with gate fees were found to be a promising feedstock for the process. More developments for catalyst stability and affordability as well as improvements in hydrogen yields are necessary to make the process commercially viable. The study noted that the promising feeds were carbohydrate-rich organic wastes and wastewaters, which could potentially reduce the H2 selling price to <0.6 $ kg1 for wastewater streams associated with a gate fee.

While hydrothermal gasification to produce hydrogen from a variety of biomass has been examined in laboratory-scale experiments (Elliott, 2009), very few pilot-scale studies have been reported at sub-critical temperatures. Like anaerobic digestion, the reported studies are mostly focused on producing methane with clean water as a by-product. Some studies are done to produce hydrogen under sub-critical conditions using a catalyst. However, just like the fermentation process, poor yield for hydrogen was obtained. The two-step approach is attractive because it focuses on hydrogen production from complex feedstock such as starch and sugar beet pulp with clean water as a by-product.

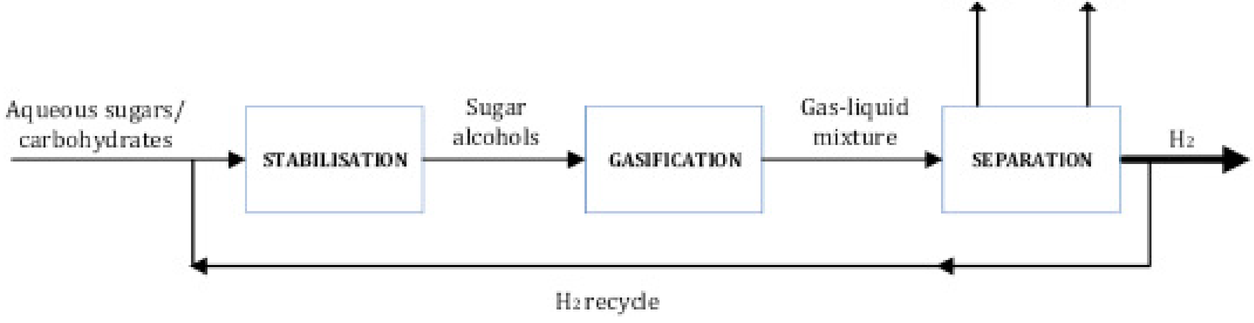

Figure 1.7. Scheme of the two-step approach to hydrothermal gasification (Paida et al., 2019, 25524-25541).

The production of hydrogen from hydrothermal gasification of biomass gets more interesting when the process is operated under supercritical conditions of water. Gasification of biomass under supercritical water conditions generates a significant amount of hydrogen. Under these conditions, phase differentiation between gas and liquid for water disappears and water acts as a solvent, reactant, and catalytic precursor in the process. Under supercritical conditions, the dielectric constant of water becomes low enough to be able to dissolve organic compounds (Tushar et al., 2020, 15390-15401). Through a combination of water–gas shift, hydrolysis, and pyrolysis reactions, the process generates an exceptionally high level of H_2 production when compared with conventional gasification (Reddyy et al., 2014, 6912-6926). Furthermore, catalysts are viable options to get better gas and H_2 yields (Calzavara et al., 2005, 615-631; Azadi and Farnood, 2011, 9529-9541; Elliott, 2008, 254-265). Nickel (Ni) catalysts are known to favor water–gas shift reactions during the gasification process, which enhances H_2 production. Ruthenium (Ru)-based catalysts have also been found to be highly effective in the gasification of biomass (Osada et al., 2012, 3179-3186). Furthermore, the Ni catalyst with Ru as a promoter shows better H_2 yields in comparison to the Ni or Ru catalyst alone (Barati et al., 2014, 140-148). Single metal on dual support or dual metal on single support catalysts were also investigated by many researchers (Calzavara et al., 2005, 615-631; Elliott, 2008, 254-265; Osada et al., 2012, 3179-3186). Tushar et al. (Tushar et al., 2016, 119-132) showed that for liquefied cattle manure (CM) a novel dual-metal support catalyst improved hydrogen yield.

Tushar et al. (Tushar et al., 2020, 15390-15401) performed supercritical water gasification of crude from cattle manure (CM) and corn husk (CH) at different conditions and compared the results with each other. The study considered three scenarios; uncatalyzed feedstock, catalyzed with 10% Ni–0.08% Ru/Al_2O_3, and finally catalyzed with 10% Ni–0.08% $Ru/Al_2O_3–ZrO_2$. Furthermore, as an industry benchmark, Al_2O_3-supported catalyst was also tested. ZrO_2 was used because it helps gasify carbon through reforming during the gasification process (Kuznetsova, et al., 2004, 161-164; Dong et al., 2004, 223-229). HTL CH was chosen as one of the feedstock because it is an ideal material for fuel generation as a byproduct of food production and it has high moisture content. The results of the study showed that 10% Ni–0.08% $Ru/Al_2O_3–ZrO_2$ performed significantly better than the other two scenarios over the 5-hour run time with a 193 and 187% higher hydrogen yield compared to the uncatalyzed and 10% Ni–0.08% Ru/Al_2O_3 catalyzed scenarios, respectively. High phenol and furan contents in the corn husk biocrude deactivated the catalyst resulting in a drop in hydrogen yield. The study also showed that the carbon gasification efficiency of the biocrude was independent of temperature. In terms of carbon conversion, the equilibrium conditions for the biocrude considered were attained at a lower temperature. Based on the Eley–Rideal model, the dissociation of adsorbed oxygenated hydrocarbon was found to be the rate-determining step.

It is a well-established fact that beyond the critical point [supercritical water (SCW), T_c = 373.95 °C, and P_c = 22.06 MPa], water becomes very reactive (Tushar et al., 2020, 15390-15401). Water under these conditions is in a single phase, which allows it to overcome any mass-transfer limitation during the gasification process and therefore has faster reaction rates. It can be used for wet biomass containing more than 70% moisture content which alleviates the cost and time required for drying biomass. Some of the cost of heating to remove water is also recoverable in a heat exchanger system (Tushar et al., 2020, 15390-15401). SCWG is flexible in terms of producing either H2-rich or CH4-rich gas depending on the operating conditions. Carbon dioxide (CO_2), produced as a byproduct of SCWG, can be sequestered or may be used in industries and chemical processes. Figure 1.8 shows the scheme of low-grade biomass conversion through the SCWG process. It also illustrates a plausible scheme for the supercritical water gasification process.

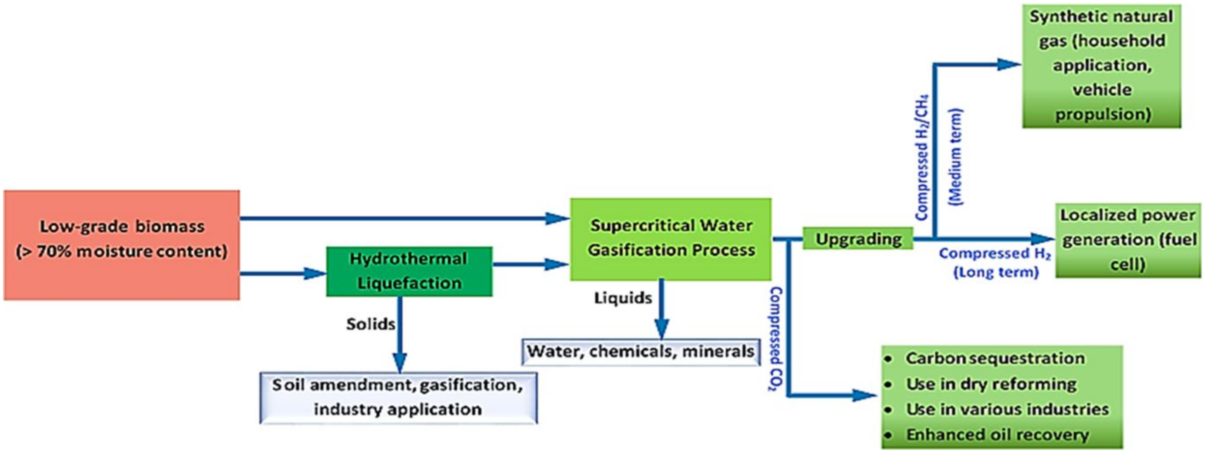

Figure 1.8. Plausible scheme of biomass SCWG process (Tushar et al., 2020, 15390-15401).

Yan et al. (Yan et al., 2006, 1515-1528) reported that SCW acts as a catalyst because of high H^+ and OH^- ions. As the product gas can be discharged at high pressure, the need for compression for storage or any downstream operations is eliminated (Ortiz et al., 2015, 634-642). Extreme temperature and pressure in SCWG create some material corrosion problems and in general more expensive than sub-critical operation. More research is needed for its fundamental understanding and better reactor and process design. A better understanding of the parameters that affect its hydrogen yield and gas composition is also required. While it is more expensive, compared to biochemical processes, it is faster, sustainable, and environment friendly and produces more hydrogen than biological processes, and requires further evaluation (Al-Mosuli et al., 2014, 445-471). More discussion on supercritical water biomass gasification is given in my previous book (Shah, 2017).

1.5.2 Reforming

The steam reforming of natural gas is the most mature technology and common process to produce hydrogen around the world [Ganguli and Bhatt, 2023, 1143987; Chen et al., 2020, 858-869; Boretti and Banik, 2021, 2100097; Franchi et al., 2020, 10-19]. It consists of the catalytic reaction of methane with steam to produce syngas, which is a mixture composed of H2 and CO. In general, this reaction is carried out using a nickel-based catalyst, and under temperature and pressure ranging between 700-900°C and 3-25 bar respectively. In order to further increase the amount of hydrogen, the syngas is submitted to a water-gas shift reaction, where H2 and CO2 are the products. Finally, the resulting gas stream (rich in H2) is subjected to separation/purification by means of the pressure swing adsorption (PSA) process, to obtain the desired hydrogen purity according to its end-use [Ganguli and Bhatt, 2023, 1143987; Chen et al., 2020, 858-869; Boretti and Banik, 2021, 2100097; Franchi et al., 2020, 10-19].

Large-scale refining and chemical industries require large reformer units (150-300 MW) with mature technologies and high efficiency(in the range of 70-85%) [Ganguli and Bhatt, 2023, 1143987; Chen et al., 2020, 858-869; Boretti and Banik, 2021, 2100097; Franchi et al., 2020, 10-19]. However, the infrastructure for a hydrogen economy, particularly for the transportation industry, requires small-scale operation (0.15-15 MW) for on-site hydrogen production [Ganguli and Bhatt, 2023, 1143987; Chen et al., 2020, 858-869; Boretti and Banik, 2021, 2100097; Franchi et al., 2020, 10-19]. The large-scale reformers which generally use packed bed systems deal with issues like pressure drop, catalyst particle size, diffusional and mass and heat transfer resistances, and the thermodynamic constraints intrinsic to equilibrium reactions [Ganguli and Bhatt, 2023, 1143987; Chen et al., 2020, 858-869; Boretti and Banik, 2021, 2100097; Franchi et al., 2020, 10-19]. In essence, the operation of large-scale reformers is heat and mass transfer limited. Small-scale or micro reformers needed for distributed hydrogen infrastructure are generally composed of a set of plates with parallel channels (diameter between 10 and 500 μm), where the catalyst is charged or coated, and where the reaction occurs. Smaller reactor configurations provide a higher surface-to-volume ratio for the catalyst, thereby minimizing mass and heat transfer resistances for the overall reaction and thus reaction becomes kinetically controlled. This kinetically controlled operation allows the possibility of improving reactor performance by improving the effectiveness of the catalyst. The large-scale reactors normally use nickel-based catalysts which are prone to coke deposition and sulfur poisoning both of which deactivate the catalyst. Small-scale or micro reformers, on the other hand, can use more active, less prone to coke deposition, and more resistant to sulfur poisoning noble metal Pt, Pd, and Rh catalysts. In the future, more cheaper catalysts would be desirable. The main challenge for micro-reformers is material selection and equipment design such that their sensitivity to fouling, pressure drop, and sealing difficulty are reduced (Ganguli and Bhatt, 2023, 1143987; Chen et al., 2020, 858-869; Boretti and Banik, 2021, 2100097; Franchi et al., 2020, 10-19).

Another interesting concept that has been extensively examined in the literature (Ramezani, 2023, 024010) is chemical looping reforming technology. In a recent study, Ramezani et al. (Ramezani, 2023, 024010) extensively reviewed this concept. CLR is considered an emerging technology with the main advantage being the indirect contact of the fuel with the oxidant by means of an oxygen transfer material. In this process, the conversion of hydrocarbon fuels into high-quality hydrogen occurs via the circulation of oxygen carriers which allow a decrease in CO_2 emissions. In the review by Ramazeni et al. (Ramezani, 2023, 024010), a comprehensive evaluation and recent progress in glycerol, ethanol, and methane reforming for hydrogen production are presented. The influence of key process variables controlling the CLR such as reactor temperature, pressure, water/fuel ratio, and CO_2/fuel ratio on fuel conversion and syngas quality are assessed. The key elements for a successful CLR process are studied and the technical challenges to achieve high-purity hydrogen along with the possible solutions are examined. The review also places special attention to oxygen carrier materials which affects product quality, cost, and the overall efficiency of the process. The use of Ni, Fe, Cu, Ce, Mn, and Co-based material as potential oxygen carriers for CLR under different experimental conditions for hydrogen generation from different feedstock is discussed. The study also reviews recent research on the sorption-enhanced reforming process. More specifically, the performances of the various types of CO_2 sorbents such as CaO, Li_2ZrO_3 , and MgO are critically reviewed.

The study concluded that methane conversion is sensitive to the operating temperature below 800 °C. While the H2/CO ratio of syngas can be adjusted by co-feeding CO2 into the fuel reactor, coke formation at the bottom of the fuel reactor exists. For glycerol reforming, with low pressure, the optimum temperature range is somewhere around 650 °C–900 °C. The design and configuration of a reactor play an important role in product yield and process efficiency. A fluidized bed presents better performance compared to a moving bed or fixed bed reactor while moving bed reactors offer better control over fuel utilization and conversions of the looping carrier. The development of the oxygen carrier with high selectivity, great stability, fast reactivity, and resistance against carbon deposition are the key aspects of the successful operation of CLR. Catalyst preparation plays an important role in reactor performance. High Ni dispersion on support, strong metal-support interaction, high catalytic activity, stability, and high resistance to carbon formation are important. While Ce-based OCs are thermodynamically favored for preferentially oxidizing methane to syngas at low temperatures, their redox stability and oxygen storage capacity need to be improved. Cu-based oxygen carriers are suitable for temperatures less than 1000 °C. They showed high oxygen transport capacity and high activity for complete oxidation of methane and strong resistance to carbon deposition. Ni is probably the best oxygen carrier for the steam reforming of glycerol. It offers high reactivity and stability during multi-redox cycles. With carbon-containing fuels, carbon formation is a significant issue with Ni-based OC. Doping an impurity and adding a proportion of steam into the fuels can inhibit carbon formation. Oxygen carrier characteristics can be improved by properly choosing the type of catalyst support, use of mixed materials, appropriate catalyst preparation methods, the addition of promoters, and modification of particle size. CaO-based solids and alkaline-based materials (Li_2ZrO_3, Li_4SiO_4, Na_2ZrO_3) are the most attractive CO_2 sorbent materials due to their application at relatively high temperatures. The SE-CLR concept has the potential to be considered an attractive technology for the production of hydrogen with H_2 purity of more than 98% and zero CO_2 emission. For commercialization of this concept, stabilization of the continuous long process operation, controlling the proper heat balance between the oxidizer and reducer, and maintaining the recyclability properties of the oxygen carriers are still remaining challenges.

Hydrogen can also be produced by “aqueous reforming at low temperatures of carbohydrates”. This process has been described in detail in my previous book (Shah, 2014). This process is slow and does have some restrictions on the carbon/hydrogen ratio of the feedstock. It is a more catalytic process than a strictly thermochemical process. Numerous types of reforming processes are also described in detail in Chapter 2.

1.5.3 Solar energy driven Thermochemical Water-Splitting Cycles

Thermochemical water decomposition is one of the promising methods of hydrogen production on large scales. In this method, water is dissociated into hydrogen and oxygen through intermediate chemical reactions. Depending on the characteristics of the thermochemical cycle, the process can utilize both thermal and electrical energy to drive the water decomposition process. Thermochemical water decomposition is a vast area including various types of cycles characterized by the number of reactions taking place in the overall cycle. Instead of a single-step thermal process demanding high reaction temperatures for complete water decomposition (around 4000 °C) (Grimes et al., 2008), employing a multi-step cycle can effectively lower the maximum required temperature for the cycle while extending the application and feasibility of thermochemical hydrogen production.

Earlier work on this subject with about 300 cycles was reviewed in detail in my previous book (Shah,2014). The book pointed out that this multi-cycle concept would avoid the Carnot cycle, as this is the fundamental difficulty in reducing the price of hydrogen production by the electrocatalytic method. The thermocycling method was assumed to cut the cost of hydrogen production by the electrocatalytic method by half. As pointed out in my previous book (Shah,2014), this assumption was later found to be fallacious. In spite of that, because the concept carries some inherent advantages, significant research has been conducted. El-Emam et al. (El-Emam et al., 2020, 121424) provided an update on emerging thermochemical cycles for nuclear-based hydrogen production. The study provides data regarding the estimated cost of hydrogen and information concerning the main safety features for integrated nuclear hydrogen production with the selected thermochemical cycles. Babu et al. (Babu et al., 2014,592-594) provided technical data regarding efficiencies and a brief summary of thermochemical cycles including Copper-Chlorine (Cu-Cl), Zinc-Oxide (ZnO-Zn), Sodium-Iodine (S-I), Calcium-Bromide (Ca-Br) and Iron-Chlorine (Fe-Cl). Yadav and Banerjee (Yadav and Banerjee,2016,497-532) conducted a review study on solar-based thermochemical cycles for hydrogen production. Experimental demonstrations, reactor technologies, and analyses of cycles from thermodynamic, economic, and life cycle perspectives are overviewed in the study.

Das and Peu (Das and Peu, 2022, 11206) comprehensively investigated and discussed recent advancements in thermochemical cycles for hydrogen production. The study mainly concerns emerging hydrogen production technologies and evaluates the potential performance enhancement by using catalysts and CO_2 absorption materials in the cycles. Mehrpooya and Habibi (Mehrpooya and Habibi,2020,123836) conducted a critical review of hydrogen production via thermochemical water splitting. Thermochemical cycles including S-I, Cu-Cl, Mg-Cl, Fe-Cl, V-Cl, and Zn-S-I are evaluated technically and discussed for their potential challenges and opportunities. The study also presents energy and exergy efficiencies as well as hydrogen production costs of some selected thermochemical cycles. Dincer and Safari (Dincer and Safari,2020, 112182) conducted a comparative assessment of various thermochemical cycles for hydrogen production in the scope of a review study. The thermochemical water-splitting cycles regarding Cu-Cl, S-I, Fe-Cl, Mg-Cl, and HyS are comparatively evaluated in terms of energy and exergy efficiencies, production cost, and global warming potential (GWP). An extensive review of two-step, three-step, and multi-step thermochemical cycles available for hydrogen production is given in my previous book on thermal energy (Shah, 2017) and by Abdin et al. (Abdin et al., 2020, 109620-109635).

Solar thermochemical water-splitting cycles (TWSCs) use high-temperature solar heat to drive a series of reactions producing hydrogen with oxygen as a welcomed by-product (Safari and Dincer, 2020, 112182). The chemicals used are recycled, creating a closed-loop process utilizing only water as feedstock, plus solar heat. The simplest TWSC is a two-step process. The metal oxide redox reactions include one endothermic reaction and one exothermic reaction. The metal oxide is transformed first into a reduced-valence metal oxide plus oxygen.

$MO_{ox}\rightarrow MO_{red}+½O_2$ (1.2)

The reduced-valence metal oxide then reacts with H_2O producing H_2, oxygen, and the initial metal oxide.

$MO_{red}+H_2O\rightarrow MO_{ox}+H_2$ (1.3)

The metal oxide is, thus, recycled. These cycles require temperatures well above 1,500°C. A TWSC with more than two steps has been designed to deliver better performances at lower temperatures. The general electric sulfur–iodine (S-I) TWSC is the most renowned three-step TWSC (Boretti et al., 2021, 666191, Schultz, 2003). It is made up of two endothermic steps and one intermediate exothermic step.

$H_2SO_4\rightarrow SO_2+H_2O+½O_2$ (1.4)

$I_2+SO_2+2H_2O\rightarrow 2HI+H_2SO_4$ (25ºC-120ºC) (1.5)

$2HI\rightarrow I_2+H_2$ (1.6)

The first reaction is a two-step reaction as follows.

$H_2SO_4 \rightarrow H_2O + SO_3$ (400ºC-600ºC) (1.7)

$SO_3 \rightarrow SO_2 + 1/2\ O_2$ (800ºC-900ºC) (1.8)

Sink et al. (Sink et al., 2009, 109) suggest 850–900°C for the endothermic reaction (1.2), 400–500°C for the endothermic reaction (1.4), and 100°C for the exothermic Bunsen reaction (1.3). While even lower temperatures have been proposed (Russ, 2009,), the efficiency of the cycle increases by increasing the temperature of the reaction (1.2). It is η~52% at a temperature of 900°C, and η~60% at a temperature of 1,000°C (Schultz, 2003). Three reactors that are a part of the cycle are called the Bunsen reactor, Gibbs reactor, and equilibrium reactor. The separation of the H_2SO_4-HI mixture is the most critical part of the S-I cycle (Shah, 2014). Some of the disadvantages include corrosion in the reactor and difficulty in supplying solar heat. This cycle has been extensively studied (Boretti et al., 2021, 666191; Norman et al., 1982, 545-556; Anzieu et al., 2006,144-153), although technological advances are still needed. Unlike direct solar thermochemical water splitting into an integrated receiver/reactor (Chueh et al., 2010, 1797-1801) which currently has a very low TRL, the TRL of the indirect solar thermochemical hydrogen production is medium. This cycle has been investigated by several research teams because the cycle involves only liquids and gases. According to my previous book (Shah,2014), General Atomics has discovered that it is possible to separate two acids in the presence of excess iodine and water. However, an efficient separation of HI from water and excess iodine at the outcome of the Bunsen reaction still remain as issues. The high-temperature decomposition of acids is also an issue. Thermal energy storage (TES) is mandatory for the dispatchability of electricity and continuous thermochemical hydrogen production. Improvements in solar concentrators' technologies, and the formulation of higher-temperature molten salts/liquid metal heat transfer fluids (HTF)/heat storage fluids (HSF) are also necessary. The cycle was successfully tested in Japan to produce 45 liters of hydrogen. It was also tested in France at the capacity of 50l/h (Shah,2014).

In order to obtain such high temperatures, point-focusing solar concentrators such as parabolic dish or heliostat field and solar tower technology should be used. Parabolic dish has temperature and structural limitations. While the heliostat field has a fixed focal point at the top of the tower, it has very low optical efficiency due to its heliostat tracking and reflecting concept. Recently, Al-Maaitah (Al-Maaitah,2017; Al-Maaitah, 2019)has developed a high flux solar concentrator with a lower focal point fixed to the ground composed of nested conical reflective rings resulting in high solar concentrations and temperatures well above 1,000°C (Al-Maaitah, 2020). High-temperature and high-pressure heat transfer fluid (HTF) can be transported by inexpensive pipes to the storage tank sitting on the ground underneath the receiver or next to it since the focal point is fixed on the ground. A 10 m in diameter concentrator was built and tested in Masdar Institute Solar Platform in Abu Dhabi (UAE) where temperatures exceeding 1,000°C have been reached at the fixed focal point even at low DNI (Al-Maaitah, 2020). The commercial name given to this concentrator is ASC (Ayman Solar Concentrator). The optical efficiency of the ASC is high and reaches 91% in practice, while it is 100% theoretically like the parabolic dish. Between the different HTFs being considered, one receiving attention is $MgCl_2$-KCl (Boretti et al., 2021, 666191, Ding et al., 2018,564-576; Polimeni et al., 2018, 510-524).

Figure 1.9 presents a scheme of the upstream ASC with TES, plus the downstream TWSC. The metallic lenses focus the solar energy on the point receiver. The cold HTF from the cold TES reservoir passes through the receiver to reach the hot TES reservoir. The hot HTF then supplies the thermal energy needed by the TWSC. While the design of the ASC and TES is relatively simple, the design of the TWSC is much more complicated, requiring multiple different reactor sections and heat exchangers. The waste heat may also be recovered.

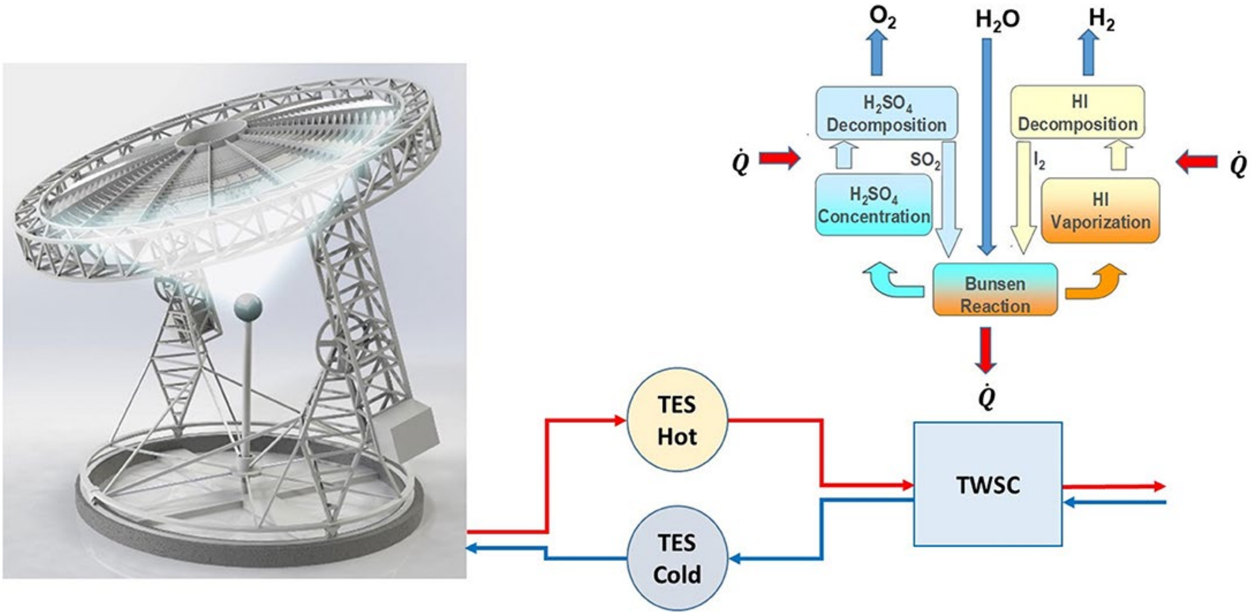

Figure 1.9 Scheme of the upstream Ayman Solar Concentrator (ASC) with thermal energy storage (TES), plus the downstream thermochemical water-splitting cycle (TWSC) (Boretti et al., 2021, 666191).

The ASC has a much better collection efficiency compared with a field of heliostat and a tower receiver. Storage can be done at high temperatures (1,100°C within easy reach). The demonstration plant is also less expensive than concentrated solar power, solar tower, and plant (Boretti et al., 2019, 10-31). With the current emphasis on green hydrogen, the technology of solar photovoltaic plus electrolysis has momentum(Boretti et al., 2021, 666191). The projected cost for this technology is 1.5 US$ per kg of H_2 by 2050. The cost can be further reduced to 1-1.5 US$ per Kg of H2, by using about the same solar concentrator and collector, plus TES, of high-temperature concentrated solar power to feed a TWSC. Kayfeci et al. (Kayfeci et al., 2019, 45-83) suggest a cost of 2.17–2.63 US$ per kg of H_2 from nuclear thermolysis. This means that this novel solar concentrator may produce thermal energy at a cost less than the cost of nuclear thermal energy and this cost is also competitive with the current steam reforming of methane without CO2 capture and storage (Boretti, 2020 3899-3904). Since ASC with TES may deliver solar heat continuously at temperatures up to 1,100°C, the use of the solar thermal process for the steps sulfur-iodine cycle appears to be a much more viable alternative than using nuclear energy. In fact, ASC with TES can be used for numerous downstream operations like hydrogen production from three-step thermochemical cycles, electricity generation, or other high-temperature thermal processes. More research is, however, needed to optimize the use of ASC with TES for TWSC (Boretti et al., 2021, 666191).

1.5.4 Photocatalytic hydrogen production from biomass

Photocatalytic production of hydrogen from biomass has been recently researched in the literature (Davis et al., 2021, 6-16; Xu et al., 2024, 108057-108071; Zhou et al., 2022, 10721-10731; Singh et al., 2023, 191-217; Yao et al., 2020, 335-348; Skillen etal., 2022, 33-46). These studies indicate that although progress has been made in regard to the photocatalytic reforming of biomass into value-added chemical substrates and molecular hydrogen, much research is needed to find active photocatalysts composed of low-cost, non-toxic materials that can sustain high rates of H2 production without the need for pretreatment of the biomass source. While metal oxide semiconductors and noble metal catalysts have established a starting point in this research, the use of metal-free semiconductor materials such as C3N4-based systems is desirable as these materials can be regenerated more effectively and economically from renewable resources. Davis et al. (Davis et al., 2021, 6-16) reported a general strategy and mechanism for photocatalytic hydrogen evolution from biomass and biomass-derived substrates (including ethanol, glycerol, formic acid, glucose, and polysaccharides). Zhou et al. (Zhou et al., 2022, 10721-10731) reviewed recent advances in biomass-based photocatalytic hydrogen production and efficient photocatalysts. The review mainly focuses on photocatalyst preparation and photocatalytic hydrogen production by using renewable biomass, biomass derivatives, and biowaste as a resource. The literature also indicates that in the past, this research field has mainly focused on light-absorbing semiconductors that depended on the absorption of UV light to drive photocatalytic activity. Recent focus has shifted to designing narrow band-gap materials and/or metal-free photocatalysts for H_2 production from biomass to improve photocatalytic performance under visible or natural sunlight and the use of mild conditions to enhance selectivity toward value-added products along with H_2 productivity.

The literature indicates that the efficiency of this process needs to be taken into consideration, as it will be a balance between renewable semiconducting resources and the efficiency that will be sacrificed to make this composite possible. The use of biomass itself, not pre-refined biomass-derived molecules, as the electron-donating substrate in the photocatalytic generation of hydrogen gas is crucial to the realization of an industrially and environmentally relevant process. In regard to foundational mechanistic studies, much is still to be desired, and the results of these future studies will determine the absolute optimal reaction conditions to photo-reform biomass into specific platform molecules or for biofuel applications. Xu et al. (Xu et al., 2024, 108057-108071) showed that despite recent studies demonstrating the feasibility of using biomass or its derivatives as electron donors in the HER, two major issues for photocatalytic conversion of biomass to hydrogen remain to be resolved: changes in the biomass structure after photocatalytic reactions and optimization of hydrogen production. The study showed that compared to single biomass components, complex biomass such as LB and its original form undergo chemical and structural changes that are difficult to directly confirm using high-performance liquid chromatography or gas/liquid chromatography-mass spectrometry in photocatalytic reforming processes. Additionally, there is a lack of efficient photocatalysts for biomass photocatalytic reforming, and most of the relevant research is still at the laboratory scale. Therefore, to promote the commercial application of this technology, there is an urgent need to develop photocatalysts that can simultaneously achieve efficient hydrogen production and precise control of liquid products.

The literature also showed that photocatalysis offers the potential to replace the energy-intensive approach of thermally reforming biomass for hydrogen production using abundant and free solar energy. Developing strategies using earth-abundant elements to form the light absorbers and photocatalysts for the capture and conversion of solar energy to electric potential energy, and eventually chemical potential energy in the form of the H–H bond, presents a key challenge in this field. As a carbon-free, energy-dense material, hydrogen will likely play an important role in mankind's energy economy of the future. Solar-driven photochemical biomass conversion presents a possible method of supplying H2 in a sustainable and climate-neutral way.

Xu et al. (Xu et al., 2024, 108057-108071, Yao et al. (Yao et al., 2020, 335-348) and Skillen et al. (Skillen etal., 2022, 33-46) make some recommendations for the future work. Xu et al. (Xu et al., 2024, 108057-108071) indicate that future research should focus on changing the physical and chemical properties, such as crystal and spatial structures, surface conditions, and chemical composition, to fully utilize solar energy, enhance charge migration rate, and reduce charge recombination. The effects of initial pH, reaction temperature, and solvent medium on H2 production in photocatalytic reforming of biomass should be investigated with significant attention to the impact of liquid products and by-products produced during the photocatalytic reforming process on the photocatalytic activity. The study also indicated that developing appropriate methods for biomass or large biomass molecule depolymerization is crucial for improving photocatalytic H2 evolution. In order to reduce the detrimental effects of by-products and pollutants on the process, the development of efficient, non-toxic, and environmentally friendly catalysts is key, particularly for certain photocatalysts such as CdS, which, despite their good photo-reforming activity, still need to address their environmental toxicity. Finally, more effort is needed to understand the relationship between HER and biomass oxidation. Generally, biomass participates in oxidation reactions by consuming oxygenic substances as reducing agents. The oxidation capability of the photocatalyst affects the pathway of biomass oxidation, thereby influencing the overall production efficiency of photocatalytic H2 evolution. Therefore, the relationship between H2 generation and biomass oxidation should be analyzed using relevant characterization methods, reaction pathways, and mechanisms.

Skillen et al. (Skillen etal., 2022, 33-46) suggested more research on catalyst synthesis for materials that are both solar-activated and economically viable for commercial production. In addition, reactor engineering must focus on the design of systems that enhance biomass substrate–catalyst interactions while promoting potential pilot-scale deployment. Beyond this, whole-systems analysis (i.e., LCA and TEA) and technology integration (i.e., wind-powered LED arrays) must come to the forefront of photocatalysis research and should be accompanied by accurate and representative metrics that act as evaluation tools to enhance stakeholder engagement across academia and industry.

Yao et al. (Yao et al., 2020, 335-348) suggested that research should be carried out for design and synthesis of novel materials and modification of methods to improve photocatalytic activity. As before they also suggested possible approaches including the modifications of existing photocatalysts to narrow their band gap and the preparation of new materials with a narrow band gap. This can be achieved by doping, noble metal nanoparticles loading, and fabrication of heterojunction. More work should be carried out with g-C3N4 and bismuth-based semiconductors (BiOBr, Bi_2WO_6, $BiVO_4$, etc.). More advanced material characterization techniques, as well as simulation methodologies, should be adopted to acquire insight into the photocatalytic process. More work should be carried out on larger-scale photocatalytic reactors. Finally, standards should be established to evaluate the performance of different materials on the same standard platform. This will guide the direction of future work. A brief summary of some of the reported studies on photocatalytic production of hydrogen is summarized in Table 1.2 as illustrated by Yao et al. (Yao et al., 2020, 335-348).

Table 1.2 Summary of photocatalytic reforming of biomass for hydrogen evolution (Yao et al., 2020, 335-348).

Catalyst	**Biomass**	**Efficiency**	**Light**
Pt-TiO_2-W	1.25 mmol/L glucose	1.0 mmol h^{-1} g_{cat}^{-1}	sunlight
Pt/P25	20 vol% methanol, 20 vol.% propanetriol, 1.3 mmol/L glucose	0.749, 7.094, 7.784 mmol h^{-1} g_{cat}^{-1}	300 W Xe lamp
Pd/TiO_2	250 mg/L glucose	5.7 mmol h^{-1} g_{cat}^{-1}	125 W high-pressure mercury lamp
Rh/TiO_2	1.25 mmol/L glucose	1.5 mmol h^{-1} g_{cat}^{-1}	300 W Hg lamp
NiS/CdS	0.10 g/L lignin & 2.0 vol.% lactic acid	1.5 (both lignin and lactic acid) & 1.086 (only lactic acid) mmol h^{-1} g_{cat}^{-1}	300 W Xe lamp
CdS/MoS_2	0.1 mol/L glucose	55.0 mmol h^{-1} g_{cat}^{-1}	300 W Xe lamp
O-g-C_3N_4	1 mol/L glucose	1.37 mmol h^{-1} g_{cat}^{-1}	simulated solar light
ZnS-g-C_3N_4	50ppm glucose	69.8 µmol h^{-1} g_{cat}^{-1}	300 W Xe lamp
S, N-GO	0.35 mol/L Sugar & 0.35 mol/L glucose	12.5 & 8.75 µmol h^{-1} g_{cat}^{-1}	300 W Xe lamp
$Bi_{0.5}Y_{0.5}VO_4$	1 mol/L glucose	50µmol h^{-1} g_{cat}^{-1}	350 W Xe lamp

1.6 Biochemical Processes for Hydrogen Production

Biomass like waste, wood, agricultural crops, and human or animal residues can be converted to hydrogen by a number of biochemical processes such as dark fermentation, direct and indirect biophotolysis, photo fermentation, anaerobic digestion followed by reforming [Fonseca et al., 2018,1-18]. Among these, dark fermentation and anaerobic digestion exhibit major developments and offer the most promising options for the biochemical production of hydrogen [Luque et al., 2016, Stolten and Emonts, 2016. In dark fermentation, an anaerobic bacterium acts over the organic matter to produce a gas stream composed of H2 and CO2. The main advantages of this process are the use of a wide variety of waste as feedstock, its simple reactor technology, and its flexibility to operate under nonsterile and impure conditions without negative effects on the performance of the process [Fonseca et al., 2018,1-18]. Process, however, accumulates by-products in the reactor and requires difficult hydrogen purification. On the other hand, anaerobic digestion is a biochemical process where different types of microorganisms metabolize the organic compounds of biomass to produce biogas (a mixture of CH4 and CO2), which is then subjected to a reforming process for hydrogen synthesis [Luque et al., 2016]. This process is described in detail in Chapter 5.

Unlike other methods, biological hydrogen production could use various raw materials and natural bacteria under normal environmental conditions of temperature and pressure(Chai et al., 2022, 392-410; Chen et al., 2020, 5053-5073). Its conversion efficiency is high and its cost is low. Biological hydrogen production includes a variety of pathways such as biological photolysis (direct and indirect), fermentation (such as dark fermentation and photo-fermentation), microbial electrolysis, etc.(Sekoai et al., 2019, 380-397). Since different biological operations depend differently on operating conditions such as substrate concentration, pH, temperature, etc., each process needs to be optimized to obtain the maximum hydrogen production. Biophotolysis uses sunlight energy directly or indirectly to generate hydrogen. Microbial electrolysis requires a much smaller amount of electricity than the electricity demand for the electrolysis of water(Sekoai et al., 2019, 380-397). The different microbial fermentation pathways are mainly dictated by the different bacteria and substrates and they will produce hydrogen in normal physiological activities under light or dark conditions. In order to stimulate the enzymatic activity of bacteria, the introduction of noble and transition metal nanocatalysts is crucial. A rational catalyst design should be selected and designed according to the required functions.

1.6.1 Dark fermentative hydrogen production

Dark fermentative hydrogen production (DFHP), is the process in which facultative and obligate anaerobic bacteria act on organic matter in the absence of oxygen and light to produce hydrogen through a series of reactions. DFHP uses dairy wastewater and kitchen waste lignocellulosic biomass as substrates for carbon sources and *Enterobacter* and *Clostridium* as the main bacteria. As shown in Figure 1.10 (Chai et al., 2022, 392-410; Tiang et al., 2020, 13211-13230) and in equations (1.9) and (1.10), two major pathways for hydrogen production are acetate fermentation and Butyrate fermentation, where H_2 is formed by disposing of excess electrons. Under anaerobic conditions, protons (H^+) act as the electron acceptor, thus producing H_2 by neutralizing the electrons produced by the oxidation of organic substrates. Whereas in aerobic respiration, oxygen is the electron acceptor and the end product is water (Chai et al., 2022, 392-410; Ghimire et al., 2015, 73-95). The process produces 4 mol H_2/mol glucose by acetate fermentation and 2 mol H_2/mol glucose by butyrate fermentation.

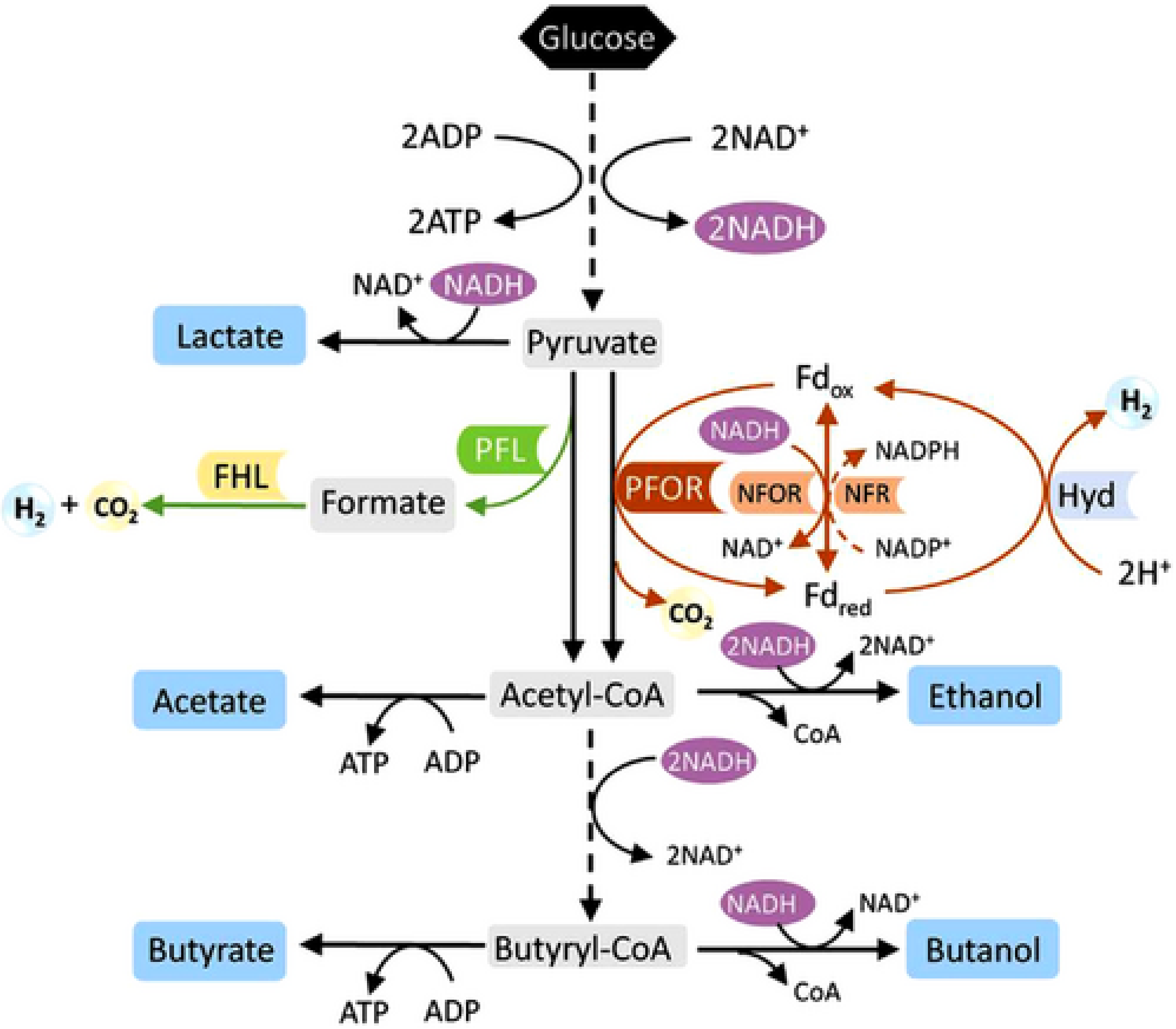

Figure 1.10. Metabolic pathways in the dark fermentative H_2 production. Reproduced with permission. Copyright 2020, Wiley (Chai et al., 2022, 392-410)

Acetate fermentation

$$C_6H_{12}O_6+2H_2O \rightarrow 2CH_3COOH+4H_2+2CO_2 \quad (1.9)$$

Butyrate fermentation

$$C_6H_{12}O_6+2H_2O \rightarrow CH_3CH_2CH_2COOH+2H_2+2CO_2 \quad (1.10)$$

The hydrogen production capacity of acidogenic bacteria is primarily used to degrade organic compounds into alcohols and volatile fatty acids (VFAs). Hydrogen production capacity and metabolism of fermentation microorganisms can be inhibited by hydrogenase activity, excessive substrate, trace elements, metal ions, temperature, pH, and toxic substances (Chai et al., 2022, 392-410). Hydrogen yield can be improved by the pretreatment of the substrate, redesign/retrofitting