

# **Preliminary study on development potential and utilization ways of hydrogen energy in municipal wastewater treatment plants**

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# Chapter I Investigation on Hydrogen Production and Development

## Introduction

With the rapid development of China's economy and society, the total demand for energy consumption is rising, and the dependence on imports of primary energy such as oil and natural gas continues to rise. High dependence on energy imports has become a huge hidden danger of China's energy security, so the transformation of energy structure is imperative. Hydrogen is one of the most abundant elements in the universe, which makes up 75% of the mass of the universe and ranks third on Earth. Hydrogen mainly exists in the form of water on the earth, so the raw materials for the preparation of oxygen are easy to obtain, and hydrogen is mainly produced by reacting with oxygen to release chemical energy. The whole energy supply process is free of waste and pollution. As a kind of secondary energy with a wide range of sources, green and efficient, hydrogen will become an important part of China's energy system in the future, and help to improve some problems existing in China's energy situation. At the same time, all aspects of hydrogen production, storage and utilization can produce huge commercial and social value, which is of great significance to China's industrial upgrading and sustainable economic development. In addition, the significance of developing hydrogen energy in China is <sup>[1]</sup>:

(1) Response to global climate change: On December 12, 2015, the Paris Climate Change Conference adopted the "*Paris Agreement*". Its main goal is to control the global average temperature rise within 2°C in this century and the global temperature rise within 1.5°C above the pre-industrial level. As a responsible country, China will make due contributions to the control of carbon dioxide and other greenhouse gas emissions, while making a good example for other countries and regions.

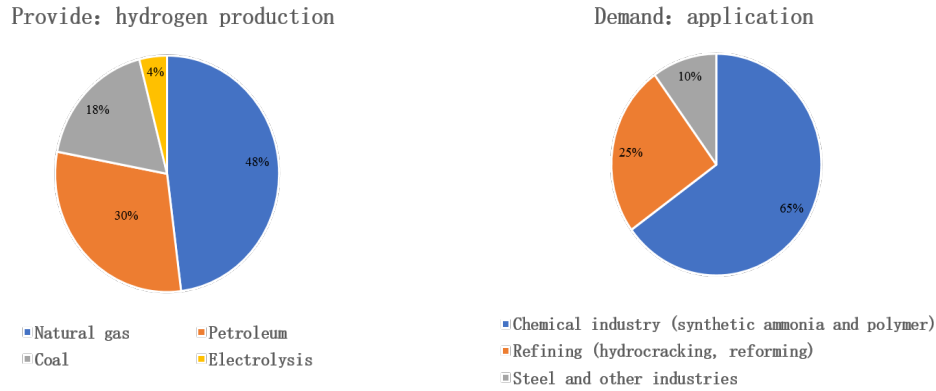
(2) Clean, efficient and pollution-free: Hydrogen, as a clean energy, not only has a wide range of sources, high combustion calorific value, no pollution and many forms of utilization, but also is expected to become the future star in the field of energy, which is called “ultimate energy” by some experts in the industry. Hydrogen is the highest calorific value of common fuels ( $142\text{KJ}\cdot\text{g}^{-1}$ ), about three times as much as oil and 4.5 times as much as coal. This means that the same mass of oil, coal and hydrogen are consumed, the hydrogen provides the largest energy, which is one of the important factors to meet the lightweight of automobiles, aerospace and other. At present, hydrogen as an energy carrier, its biggest competitor is the battery. In addition, the theoretical specific energy of hydrogen is  $142\text{ KJ}\cdot\text{g}^{-1}$ , which is 71 times the theoretical specific energy of lithium battery ( $555.5\text{ Wh}\cdot\text{kg}^{-1}$ ). Even with the hydrogen storage materials (calculated at 5.4% of the current capacity, it will continue to increase in the future), the theoretical specific energy of hydrogen can reach  $2130\text{ Wh}\cdot\text{kg}^{-1}$ , which is more than 3.8 times of lithium battery. And the operating temperature of hydrogen is not limited (battery operating temperature range is about  $20^{\circ}\text{C} \sim 60^{\circ}\text{C}$ ). In summary, the development of hydrogen energy will play an important role in China’s industrial upgrading.

(3) In terms of energy security: Taking Japan, for example, Japan has a first-mover advantage in the utilization of hydrogen energy. One of the most important considerations is the energy security. Japan’s energy is heavily dependent on overseas supply. In the future, their energy development direction will focus on compressing the development of nuclear power, reduce the dependence on fossil energy, and then promote the development of renewable energy by the government. China should also learn from Japan’s experience to ensure China’s energy security. Hydrogen exactly can meet this demand.

For decades, hydrogen energy has been used as raw material for industrial production, and relevant markets have been well established. According to the report of the Hydrogen Energy Council, the global demand for hydrogen energy in 2015 was 8EJ, and the market size of hydrogen energy raw materials was about USD 115 billion. By 2022, the market size will reach USD 255 billion. But it needs to be pointed out that although “hydrogen energy-fuel cell-automobile” is a technically feasible energy use plan, and the gradual opening of the downstream



application market has also promoted the balanced development of the entire industry chain, at present, however, the hydrogen energy is not widely used as motor vehicle fuel.



**Figure 1.1 Schematic diagram of global hydrogen supply and demand**

The development of hydrogen energy in China has its own characteristics. The list of major hydrogen production enterprises in China is shown in table 1.1. It can be seen from the table that hydrogen is mainly produced from fossil energy in China. And hydrogen production enterprises are mostly state-owned enterprises and other large enterprises. It shows that the hydrogen industry has a high threshold and requires the adequate financial and technical support. In order to facilitate in-depth understanding of China's hydrogen industry, this paper summarizes some of the basic situation and development of the main hydrogen production mode for reference.

**Table 1.1 Summary of top ten domestic hydrogen production enterprises, the production methods and production capacity <sup>[2]</sup>**

Rank	Enterprise	Hydrogen production method	Hydrogen production( $\times 104t/\text{year}$ )
1	CHN ENERGY	Coal to hydrogen	400
2	China Fossil	Hydrogen production unit, hydrogen by-product of refining and reforming, and hydrogen by-product of ethylene production	200~300
3	Huachang Chemical	Sodium borohydride hydrogen production	20
4	Oriental Energy	PHD (Propane Dehydrogenation)	6
5	Meijin Energy	Coke oven gas by-product hydrogen	5.9

6	Jinneng Technology	PHD (Propane Dehydrogenation)	4.1
7	Weixing Petrochemical	PHD (Propane Dehydrogenation)	3
8	Juzhengyuan shares	PHD (Propane Dehydrogenation)	2.8
9	Hongxing daye	Hydrogen by-product from chlor-alkali industry	2.5
10	BEFAR GROUP	Hydrogen by-product from chlor-alkali industry	1.7

In fact, the current classification of hydrogen production methods is not very uniform, which is classified according to the source of raw materials, including hydrogen production from by-products of chlor-alkali industry, hydrogen production from electrolytic water, hydrogen production from chemical raw materials (including methanol cracking, ethanol cracking, liquid ammonia hydrogen production), and hydrogen production from fossil resources (including oil cracking, water gas, etc.). There are also classifications based on the transformation mode, such as light conversion to hydrogen, electric conversion to hydrogen, thermal conversion to hydrogen, etc. In this paper, the main hydrogen production methods and related contents will be introduced mainly according to the source of raw materials.

# 1. By-product hydrogen from chlor-alkali industry

## 1.1 Overview

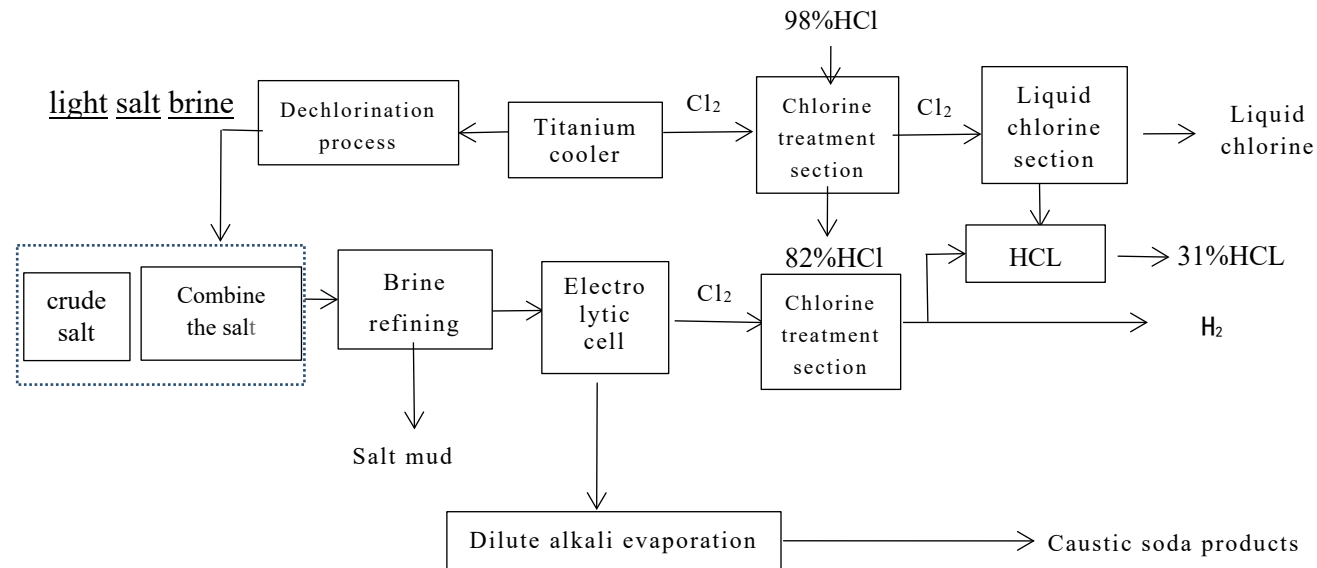
Using salt water (sodium chloride solution) as raw material, caustic soda, chlorine gas and by-product hydrogen were produced by ion membrane or asbestos diaphragm electrolyzer in chlor-alkali plant. There are many impurities such as hydrogen containing chlorine in the by-products of chlor-alkali industry, and the purity is relatively low, so the use is limited. This method also has its advantages: low cost [3]. Most chlor-alkali plants adopt the physical adsorption PSA method to purify the by-product hydrogen, and obtain high-purity hydrogen. This process has the advantages of low energy consumption, low investment, high automation, high product purity no pollution. Considering that the purity of the by-product hydrogen is over 99% before purification, and the main impurities are oxygen, nitrogen, and water vapor, the production cost of high-purity hydrogen under this process is only 1.3~1.5 yuan·Nm<sup>-3</sup>. At present, the utilization of hydrogen in chlor-alkali plants mainly includes two aspects. One is the reaction with chlorine to generate hydrochloric acid, and the other is the direct combustion of hydrogen to generate heat energy. But the latter requires a lot of investment, so many chlor-alkali plants actually emptied hydrogen directly. This is a waste of hydrogen resources in essence. If the hydrogen produced by chlor-alkali plants can be collected reasonably, it will be a reasonable way for the development of fuel cells.

## 1.2 Principle and process

The principle of hydrogen production from by-products of chlor-alkali industry is shown in the following formula



The purification process of common products is as follows: hydrogen is produced from the by-products of chlor-alkali industry, chlorine, sulfur and oxygen are removed sequentially, and then the high purity hydrogen is purified by PSA technology. The typical process is shown in Figure 1.2.



**Figure 1.2 Process of byproduct hydrogen production in ion-membrane caustic soda plant <sup>[4]</sup>**

PSA technology uses the difference of adsorption characteristics of gas components on solid adsorption materials to achieve gas separation and purification through periodic pressure changes. PSA technology is a physical adsorption method with the advantages of low energy consumption, low investment, simple process, high degree of automation, high product purity and no environmental pollution. The basic process flow is shown in Figure 1.3.

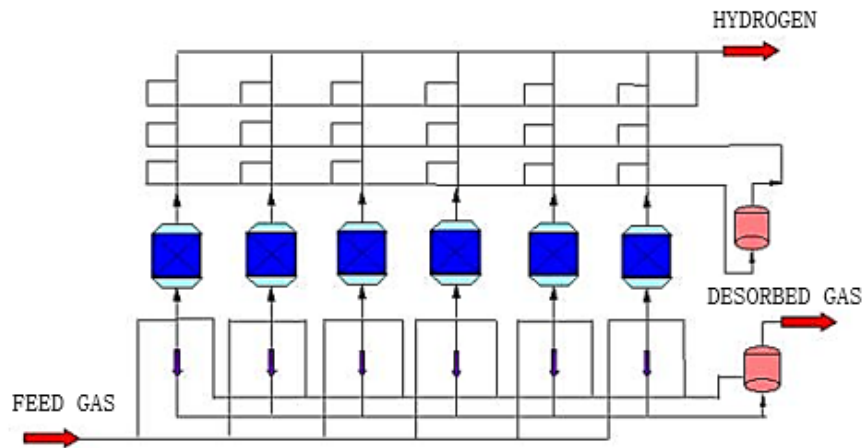


Figure 1.3 The process of Hydrogen Separation by PSA Technology <sup>[5]</sup>

### 1.3 Development statu

China is a big country of chlor-alkali production and use. Figure 1.4 shows the provinces which caustic soda production capacity greater than  $1.0 \times 10^4$  t in 2018, and the theoretical data of hydrogen production by caustic soda by-products over the years.

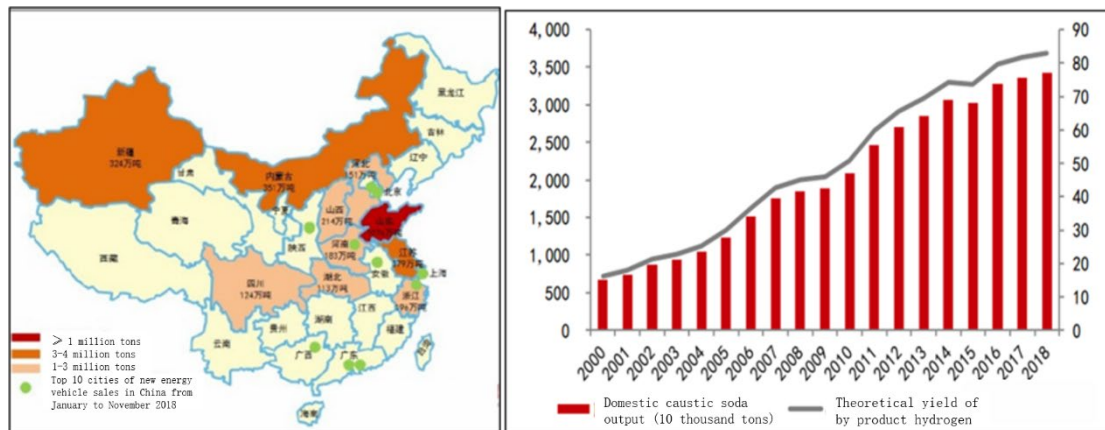


Figure 1.4 Provinces with domestic caustic soda production capacity  $\geq 1 \times 10^6$  t (left) and theoretical production of hydrogen as a by-product of chlor-alkali (right) <sup>[4, 6]</sup>

In terms of output, the domestic caustic soda production reached  $3.420 \times 10^4$  t in 2018. According to the calculation of 280 Nm<sup>3</sup> hydrogen (25 kg) per 1 t caustic soda production,  $8.55 \times 10^5$  t hydrogen per year is produced. At present, there are two ways to utilize by-product hydrogen in domestic chlor-alkali plants, one is to prepare hydrochloric acid or other chemicals by reacting with chlorine

gas, the other way is to release the heat energy from combustion (large investment in the early stage). Currently, more than 30% of by-product hydrogen is directly released, which causes a lot of waste of resources. If the released by-product hydrogen is fully utilized, the external supply of  $2.556 \times 10^5$  t high purity hydrogen can be theoretically realized, and more than  $1.00 \times 10^4$  fuel cell vehicles can be supplied, which is sufficient to meet the short-term and medium-term hydrogen demand of domestic fuel cell vehicles.

In 2019, the total amount of by-product hydrogen in chlor-alkali industry was about  $7.9 \times 10^5$  t, of which  $6.7 \times 10^4$  t of hydrogen was not effectively utilized [7]. If each hydrogen fuel cell vehicle is charged with 5 kg of hydrogen per day and travels 200 kilometers, the unused by-product hydrogen from the chlor-alkali industry in 2019 can provide about  $3.6 \times 10^4$  fuel cell vehicles for one year. In addition, the unutilized hydrogen in the chlor-alkali industry can be purified and sold to the hydrogenation station or used for enterprise self-supply. For example, in September 2016, Yingchuang Sanzheng (Yingkou) Fine Chemical Co., Ltd. used the by-product hydrogen from chlor-alkali to build a 2MW hydrogen fuel cell power station, which has achieved 20% self-supply of electricity. The technical suppliers of its fuel cell equipment are MTSA Technopower and Nedstack Fuel Cell Technology in the Netherlands. This technology has not been truly localized.

As far as the current domestic production scale, Hongxingda ( $2.5 \times 10^4$  t/year) and Befar Group ( $1.7 \times 10^4$  t/year) are both the representative by-product hydrogen production companies of chlor-alkali industry. Ranked 9th and 10th respectively in the domestic hydrogen industry. But overall, the hydrogen production by-product of the chlor-alkali industry still accounts for only a small percentage of the hydrogen production industry. 2020, Hongda xingye Industrial's wholly-owned subsidiary Inner Mongolia Zhonggu Mining Co., Ltd. and Jiangsu Jincai Technology Co., Ltd. purchased a  $3.0 \times 10^5$  t/year ion exchange membrane method large-scale electrolysis device from Japan's Asahi Kasei Co., Ltd. The device uses brine as raw material to produce the hydrogen, caustic soda and other products. The whole device includes the patent and proprietary technology licensing, process design packaging, technical documents, technical services and training, equipment, materials, catalysts, chemicals and spare parts, which also

marks that the hydrogen production from by-products of chlor-alkali industry will continue to develop to a large scale <sup>[8]</sup>.

## 2. Hydrogen production by electrolytic water

### 2.1 Overview

Hydrogen production by electrolysis of water means that when a large enough voltage is applied at both ends of the electrode, water molecules will oxidize at the anode to produce oxygen and reduce at the cathode to produce hydrogen. Therefore, the electrolysis water reaction is divided into two half reactions: anodic oxygen evolution reaction (OER) and cathodic hydrogen evolution reaction (HER). As a weak electrolyte, pure water has a low degree of ionization and poor conductivity. In the process of hydrogen production from electrolytic water, some easily ionized electrolytes are usually added to increase the conductivity of the electrolyte. Alkaline electrolytes have strong hydrogen production effect and are often used without corrosion of electrodes and electrolytic cells and other equipment. The KOH or NaOH solution with concentration of 20% – 30% are usually used as electrolyte <sup>[9]</sup>.

Due to the alkaline electrolyzed water uses non-precious metal catalysts, the operating temperature is generally 50~80°C, and the cost is relatively low. Since the discovery of the reaction in 1789, the alkaline electrolyzed water has become the most mature hydrogen production technology, with an installed capacity of up to megawatts, which is currently the most widely used and most widely distributed hydrogen production technology on the market. Its main components are porous cathode and anode, the middle diaphragm and alkaline electrolyte <sup>[10]</sup>.

### 2.2 Principle and process

As shown in Figure 1.5, the electrolysis of water for hydrogen production is based on the electrolyte being acidic and alkaline, and the principles are different.

(1) In alkaline and neutral media:

The anode reaction is:  $2\text{OH}^- - 2\text{e}^- = \text{H}_2\text{O} + 1/2\text{O}_2\uparrow$

The cathode reaction is:  $2\text{H}_2\text{O} + 2\text{e}^- = 2\text{OH}^- + \text{H}_2\uparrow$

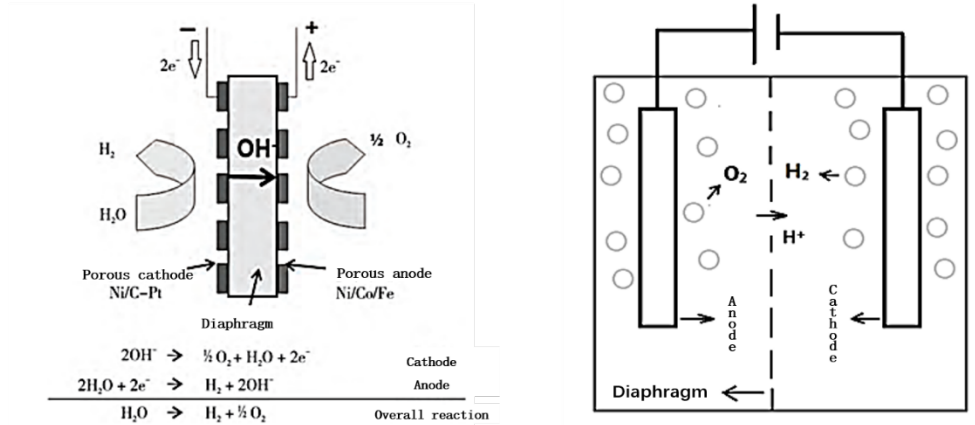
The total response is:  $2\text{H}_2\text{O} = 2\text{H}_2\uparrow + \text{O}_2\uparrow$



(2) In acidic medium: the anode reaction is:  $2\text{H}_2\text{O}-4\text{e}^-=4\text{H}^++\text{O}_2\uparrow$

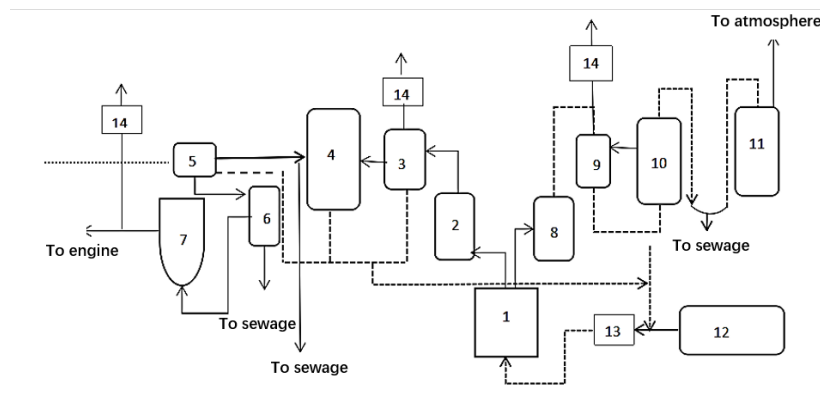
The cathode reaction is:  $4\text{H}^++4\text{e}^-=2\text{H}_2\uparrow$

The total response is:  $2\text{H}_2\text{O}=2\text{H}_2\uparrow+\text{O}_2\uparrow$



**Figure 1.5 Schematic diagram of electrolyzed water under acidic (left) and alkaline (right) conditions**

The typical process of hydrogen production by electrolysis of water is shown in Figure 1.6. It mainly includes electrolytic cell, hydrogen measurement system, oxygen side system, recharge water system, alkaline system, pure water preparation and other ancillary equipment (including hydrogen and oxygen storage, purification, compression transport equipment and related control instruments and power supply, etc.) [11].



**Figure 1.6 Flow chart of typical electrolyzed water**

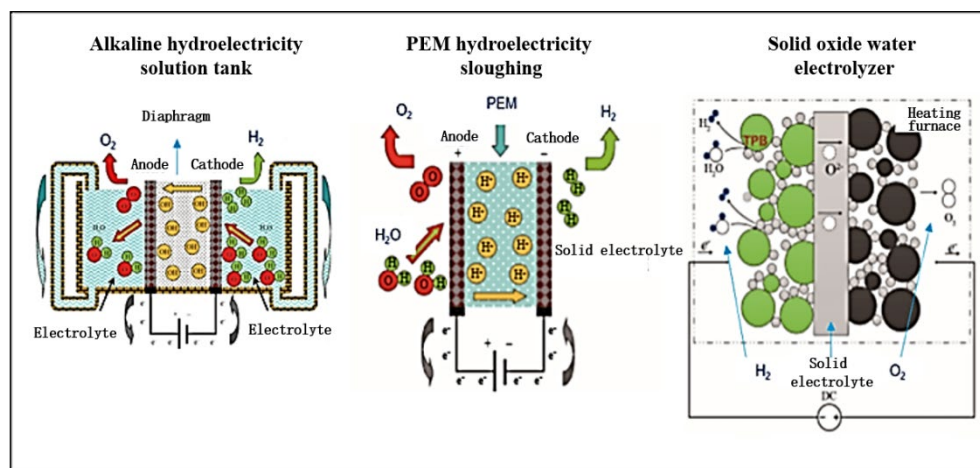
- Electrolyzer; 2-Hydrogen side separator; 3-Hydrogen side scrubber; 4-Hydrogen side pressure regulator; 5-Balance box; 6-Cooler; 7-Hydrogen storage tank; 8-Oxygen side separator; 9- Oxygen side scrubber; 10-oxygen side pressure regulator; 11-oxygen side water seal tank; 12-lye tank; 13-lye filter; 14-flame arrester

- Hydrogen side system: the hydrogen electrolyzed from each interval of electrolyzer 1 is collected in the main pipe, passes through the hydrogen measuring separator 2, scrubber 3, pressure regulator

4, balance box 5, and then passes through the two-stage cooler 6, and then is stored in the storage tank. The hydrogen tank is spare.

●Oxygen side system: The oxygen decomposed from each interval of electrolytic tank 1 is collected in the main pipe, and after the oxygen side separator 8, scrubber 9, pressure regulator 10 and water seal tank 11, it is discharged to the atmosphere or stored in a storage tank for later use.

The electrolysis cell includes the alkaline water electrolysis cell, PEM (proton exchange membrane) water electrolysis cell, and solid oxide water electrolysis cell. The working principle is shown in Figure 1.7.



**Figure 1.7 Schematic diagram of working principle of three kinds of electrolytic water electrolyzers <sup>[7]</sup>**

Alkaline electrolyzed water hydrogen production device has low cost and the most mature structure frame, so alkaline water electrolyzer is the most commercialized water electrolysis device. However, the device still has the problems of liquid electrolyte leakage and high energy consumption. The maximum gas production of single unit in China is  $1.0 \times 10^3 \text{ m}^3 \cdot \text{h}^{-1}$ . The efficiency of proton exchange membrane electrolyzer is high, but due to the use of precious metal catalysts and the slow localization process of important parts, the device cost and production cost are higher. The solid oxide water electrolysis device is still in the laboratory development stage. The comparison of the characteristics of the three specific electrolyzers is shown in Table 1.2.

**Table 1.2 Comparison of three electrolytic water electrolyzer processes <sup>[7]</sup>**

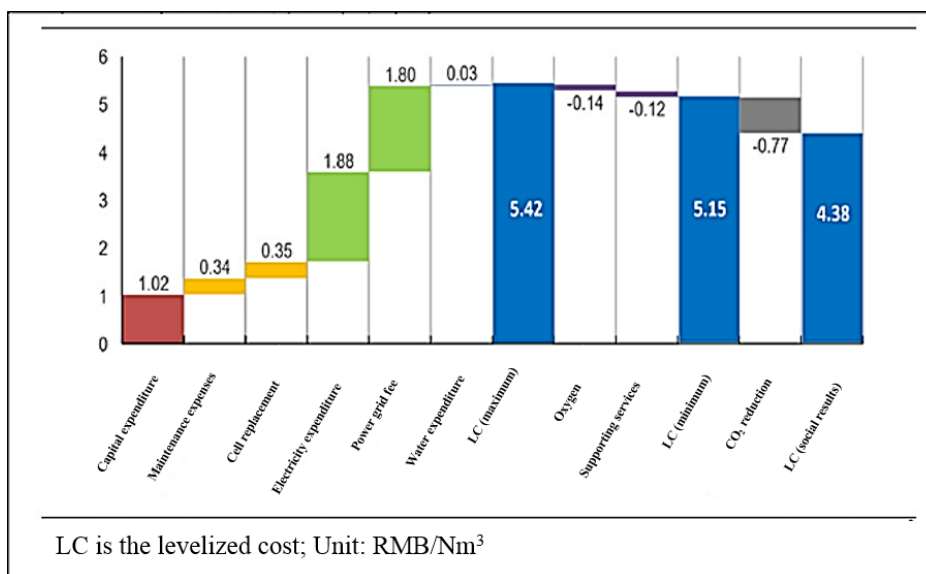
Index	Alkaline water electrolysis cell	Proton exchange membrane water electrolysis cell	Solid oxide water electrolysis cell
Energy efficiency (60%)	75~70	90~85	100
Operating temperature (70℃)	90~70	80~700	1000

Current density ( $A \cdot cm^{-2}$ )	0.2~0.4	January 2	January 10
Energy consumption ( $24.5kWh \cdot Nm^{-1}$ )	5.5~3.8	5.0~2.6	3.6
Electrolyte	20-30%KOH (liquid)	PEM (Nafion) (solid)	Y2O <sub>3</sub> /ZrO <sub>2</sub> (solid)
System maintenance cost	high	low	high
Stack life (h)	12000	10000	10000
Electrolyzer cost (yuan/kw)	2800~4200	14000	7000~10500
Technological progress	Mature technology and high degree of commercialization	Demonstration stage	Laboratory stage

## 2.3 Development status

At present, the energy consumption of hydrogen production by alkaline electrolysis of water is high, and the unit energy consumption is  $4.5\text{--}5.5kWh \cdot (m^3)^{-1}$ . The cost of electrolytic water mainly includes depreciation of assets, operating costs (general maintenance, battery replacement), and electricity costs (electricity consumption, and grid fees), among which the electricity costs account for a relatively high proportion, reaching 70%–80%. In addition, the amount of carbon dioxide produced by electrolysis water per kilogram of hydrogen is about 35.8 kg.

Figure 1.8 shows the cost distribution of hydrogen production from water electrolysis. Based on the assumption that the hydrogen production capacity is  $600 Nm^3 \cdot h^{-1}$  and the annual hydrogen production is  $1.2 \times 10^6 Nm^3$ , the hydrogen production project of electrolytic water can be calculated as follows: the annual power consumption is  $6.0 \times 10^6 kWh$ , if the electricity price is assumed to be  $0.5 \text{ yuan} \cdot kWh^{-1}$ , hydrogen is sold at  $4 \text{ yuan} \cdot Nm^{-3}$ , and the annual gross profit margin is about 28% [12]



**Figure 1.8 Cost distribution waterfall diagram of hydrogen production from electrolytic water**

The cost and production scale of hydrogen production from electrolytic water are also closely related. For different hydrogen production scale, the corresponding hydrogen cost is also different. In general, the larger the production scale is, the lower the corresponding hydrogen cost is. The hydrogen production costs calculated by a company are shown in table 1.3

**Table 1.3 Cost of hydrogen production from electrolyzed alkaline water**

Production scale (m <sup>3</sup> ·h <sup>-1</sup> )	Annual production time (h)	Electricity price (yuan·kW <sup>-1</sup> )	Proportion of electricity consumption (%)	Depreciation percentage (%)	Proportion of labor (%)	Hydrogen cost (yuan·m <sup>-3</sup> )
1000	2880	0.3	69	8.3	16	2.2
5000	2880	0.3	79.1	9.4	5.5	1.92
10000	2880	0.3	80	9.6	3.8	1.89

At present, the main technical research of hydrogen production from electrolytic water is how to reduce the energy loss in the electrolysis process and improve the energy conversion efficiency. From the current research progress, the energy consumption of commercial alkaline electrolysis water is about 4.5~5.5 kW·h·(m<sup>3</sup>)<sup>-1</sup>. Compared with the minimum energy consumption 2.95 kW·h<sup>-1</sup> calculated by thermodynamic principle, the energy efficiency is only 60% -75% [13], and there is still much room for improvement. The hydrogen production will focus on converting surplus electricity into hydrogen energy in the future. Especially for China, making good use of the world's largest wind power and

solar power to solve the intermittent problem of clean energy affected by day and night changes and climatic factors, which is an important application field of hydrogen production from electrolytic water.

In terms of development prospects, water electrolysis technology coupled with renewable energy sources has become a new breakthrough. Hydrogen production by electrolysis of water from renewable energy is an important means to solve the problem of high cost and carbon emission of hydrogen production by electrolysis. Due to the unevenness and indirectness of renewable energy power generation, grid-connected transmission is likely to cause grid fluctuations, so a large number of renewable energy sources are not connected to the grid. In 2019, when the national curtailment of wind power was  $1.69 \times 10^{10}$  kW, the average curtailment rate was 4.7%. When the waste light output is  $4.5 \times 10^9$  kW, the average waste light rate is 2%. The use of “abandoning wind, light, and water” electricity to produce hydrogen from water has become a new idea for the development of green hydrogen energy. If calculated based on the abandonment of  $0.1 \text{ yuan} \cdot \text{kWh}^{-1}$ , the cost of hydrogen production can be reduced to about  $10 \text{ yuan} \cdot \text{kg}^{-1}$ , and the cost of hydrogen production is equivalent to the cost of hydrogen production from traditional fossil fuels. And because it is green energy power generation, the carbon emission problem has basically been solved. However, due to the centralized large-scale wind power and photovoltaic power stations in China are concentrated in the northwestern region, the transportation of hydrogen produced from abandonment of electricity to the eastern and southern regions where demand is greater involves high hydrogen transportation costs and safety issues. With the development of hydrogen storage and transportation technology and the construction of hydrogen transportation network, the transportation cost of hydrogen production from renewable energy is expected to further decrease in the future. The country and the world are advancing the development of hydrogen production from renewable energy. In 2016, Hebei Construction and Investment New Energy Co., Ltd. used the experience and practices of Brandenburg, Germany in the development and utilization of renewable energy, improving the ecological environment, and cited the wind power hydrogen production technology of the German McPhy Energy Co., and planned to start the construction of “Guyuan Wind Power hydrogen production

demonstration project”. In 2019, the Zhangjiakou Hypor hydrogen production and refueling project was invested and constructed by Yihuatong Power Technology Co., Ltd., including a hydrogen production station and supporting hydrogen refueling stations. The hydrogen production station uses the hydrogen production technology of wind power electrolysis water. After the completion of the project, it is expected to achieve an annual yield of  $1.6 \times 10^7 \text{ m}^3$  of hydrogen with a purity of 99.999 %. In addition, Sichuan, Guangdong and other places have proposed electricity price support policies, the maximum electricity price for hydrogen production from electrolytic water is limited to  $0.3 \text{ yuan} \cdot \text{kWh}^{-1}$  and  $0.26 \text{ yuan} \cdot \text{kWh}^{-1}$ .

Internationally, Japan’s New Energy Industry Technology Development Organization (NEDO), Toshiba Energy Systems, Tohoku Electric Power, and Iwatani Industry have built the world’s largest (10MW) renewable energy source in Nanie-cho, Fukushima Prefecture since 2018. The FH2R (Fukushima Hydrogen Energy Research Field) demonstration project for producing hydrogen from renewable energy has been completed and put into operation at the end of February 2020. FH2R uses 20 MW photovoltaic power installed on a  $1.8 \times 10^5 \text{ m}^2$  site, electrolyzes water through a world-class 10 MW hydrogen production system, with an hourly output of  $1.2 \times 10^3 \text{ N} \cdot \text{m}^3$ , and can store and supply hydrogen, the largest in the world. In the future, the electrolyzed hydrogen production coupled with more power generation devices will likely become the mainstream hydrogen production method.



**Figure 1.9 The real scene of the FH2R project park<sup>[14]</sup>**

In addition, the Suzhou Jingli Company is also a domestic unit that mainly operates hydrogen production by electrolysis of water. It can develop, produce and sell various types of gas equipment, water electrolysis hydrogen production equipment, and various types of professional hydrogen energy equipment. The maximum single hydrogen production machine produced by it is  $1.0 \times 10^3 \text{ m}^3 \cdot \text{h}^{-1}$ , and the current annual production capacity is the largest in China (Figure 1.10). Suzhou Jingli participated in the national related 973, 863 wind photovoltaic hydrogen production scientific research projects. The use of wind power, solar energy, and hydropower to produce hydrogen will be widely used as an important means of energy storage and conversion, and it can also adjust the balance. The important role of grid load can be described as “multiple benefits with one action”.



**Figure 1.10 The electrolyzed water equipment and demonstration project of Suzhou Jingli Company**

Data shows that more and more electrolysis water hydrogen production models coupled with other power generation methods are promoted in different regions. In the future hydrogen production industry, electrolysis water hydrogen production will occupy an increasing proportion.

### **3. Hydrogen production from fossil resources**

Hydrogen production from fossil fuels includes the direct use of primary energy sources such as coal to produce hydrogen and the use of chemical raw materials to produce hydrogen. Chemical raw materials refer to the secondary raw materials formed after a certain chemical process transformation, mainly including methanol reforming to produce hydrogen, ethanol cracking to produce hydrogen, and liquid ammonia to produce hydrogen. At present, large-scale hydrogen production is still dominated by coal and natural gas. 92% of global hydrogen production uses coal and natural gas, about 7% comes from industrial by-products, and only 1% comes from electrolyzed water. At the same time, in recent years, due to the large-scale application of hydrogen production from coal and natural gas, as well as due to petroleum substitution and economic reasons, the partial oxidation hydrogen production technology of heavy oil (atmospheric and vacuum residues and fuel oil, etc.) to produce hydrogen has been rarely used in industry.

#### **3.1 Coal to hydrogen**

##### **3.1.1 Overview**

At present, there are three main routes for hydrogen production from coal: (1) Direct hydrogen production from coal; (2) Hydrogen by-product from coal chemical industry. For example, the synthesis gas from coal to methanol contains hydrogen. (3) Use coal to generate electricity and produce hydrogen through electrolytic water. Gasification of hydrogen is one of the preferred methods for large-scale industrial hydrogen production. This article mainly introduces the hydrogen production from coal gasification. The configuration of typical coal hydrogen production workshop is shown in Figure 1.11.



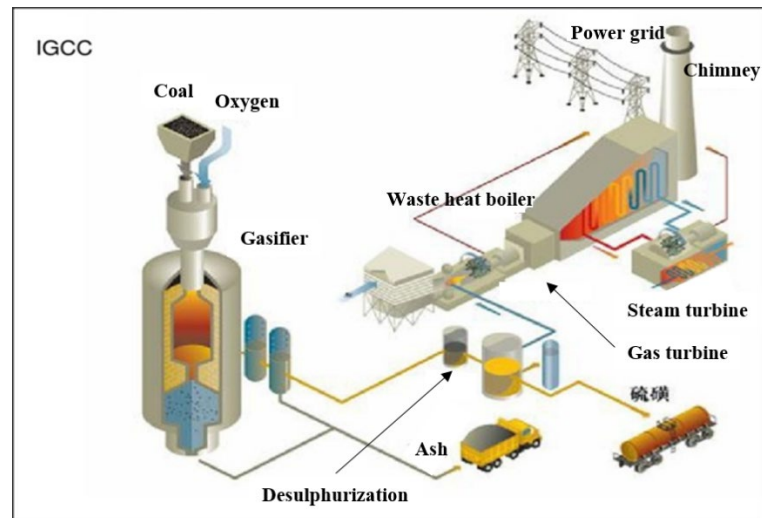


Figure 1.11 Layout of the coal gasification hydrogen production workshop<sup>[15]</sup>

### 3.1.2 Principle and process

Hydrogen production from coal gasification is a complex reaction involving multiple reactions, including partial oxidation of carbon to form CO, all oxidation to form CO<sub>2</sub>, and multi-step reactions of C and CO<sub>2</sub> to form CO. Figure 1.12 can be used to illustrate<sup>[16]</sup>.

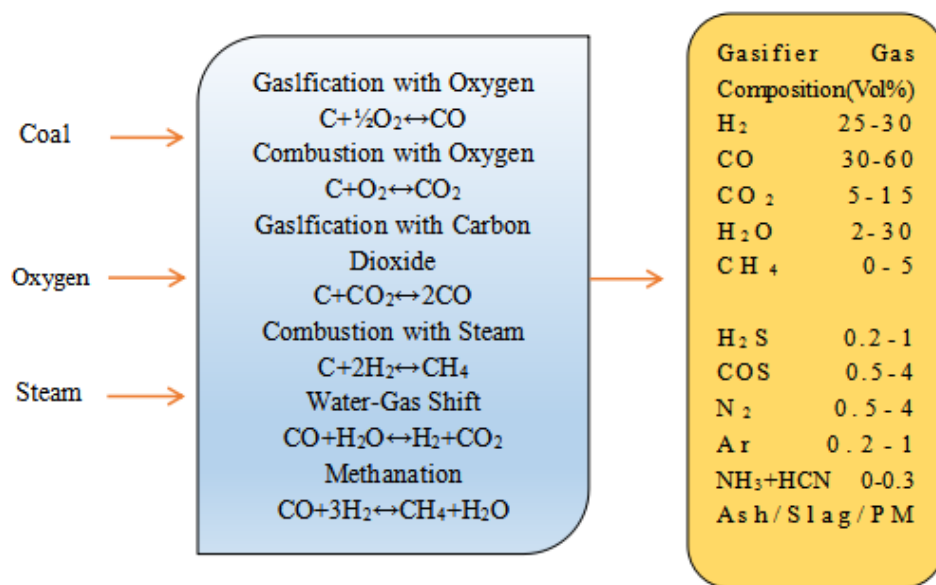


Figure 1.12 Schematic diagram of hydrogen production from coal gasification<sup>[16]</sup>

As far as the basic process is concerned, the general process of coal gasification is shown in Figure 1.13, including gas production, purification, and

transformation. The traditional coal gasification hydrogen production process has the characteristics of mature technology, low raw material cost, and large-scale equipment, but its equipment structure is complex, the operation cycle is relatively short, the supporting equipment is multiple, the equipment investment cost is high, and the gas separation cost is high, the hydrogen production efficiency is low, and the CO<sub>2</sub> emission is large.

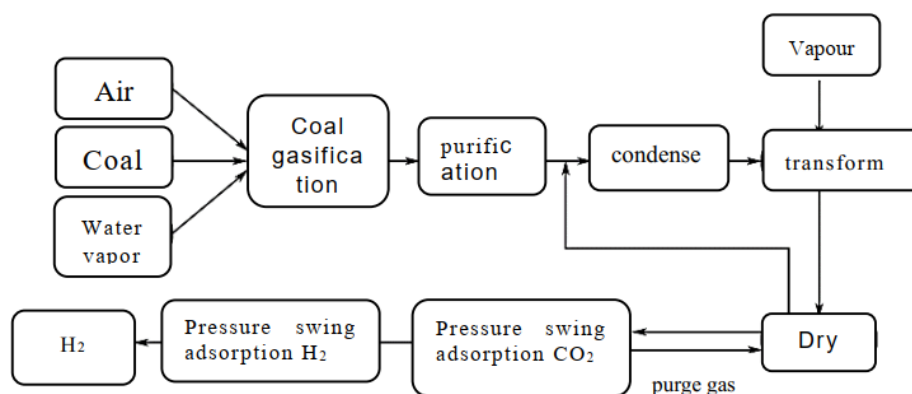


Figure 1.13 Typical process flow diagram of hydrogen production from coal gasification<sup>[17]</sup>

### 3.1.3 Development status

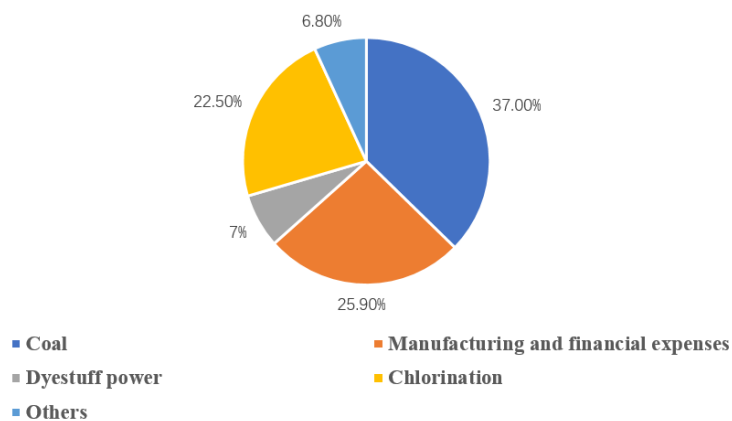
In general, hydrogen production from coal gasification has many advantages as follows: (1) Low cost. Taking 90,000 Nm<sup>3</sup>·h<sup>-1</sup> hydrogen production scale as an example, the investment in coal-water slurry gasification and natural gas hydrogen production plants are 1.24×10<sup>9</sup> yuan and 6×10<sup>8</sup> yuan, respectively. Although the investment in coal-to-hydrogen is much higher, when the hydrogen price (cost+10% return on investment) is 1.5×10<sup>4</sup> yuan·t<sup>-1</sup> (1.36 yuan·m<sup>-3</sup>), the corresponding coal and natural gas costs are 805 yuan·t<sup>-1</sup> and 2.58 yuan·m<sup>-3</sup> (converting coal or natural gas into hydrogen, and inferring the corresponding coal and natural gas prices based on the price of hydrogen), and the value of the large amount of steam produced by coal to hydrogen has not been calculated; (2) The large amount of steam produced by the coal gasification unit (waste heat boiler process) can save fuel oil in the refinery. The fuel oil saved can be used as the raw material of the coking unit to increase the production of refined oil; (3) Cheap coal production of hydrogen can replace dry gas production. The saved dry gas can be used to extract chemical raw materials such as ethylene to increase economic benefits; (4) The raw materials for hydrogen production from coal-

water slurry gasification are flexible, and the mixed feed of petroleum coke and coal can be accepted in a wide proportion range. Solve the problem of petroleum coke sales when coal prices are high and petroleum coke prices are low. When the coal price is low and the petroleum coke market price is high, all coal can be gasified to maximize the benefit <sup>[18]</sup>.

The cost of hydrogen production from coal is mainly composed of coal, oxygen, fuel power energy consumption and manufacturing costs, but the proportion of raw materials is only 37% far less than the proportion of natural gas. Generally, the coal-to-hydrogen uses a partial oxidation process, which is calculated according to the oxygen cost of the supporting air separation unit, accounting for 26% of hydrogen production. Due to the large investment in coal-to-hydrogen, manufacturing and financial costs have also become important cost-influencing factors, accounting for 23% (Figure 1.14).

At present, the more mature large-scale hydrogen production methods include coal-based hydrogen production and natural gas-based hydrogen production. Therefore, most of the data compare the costs of these two hydrogen production methods (Table 1.4). The characteristics of hydrogen production from natural gas are short process, low investment and stable operation. The characteristics of hydrogen production from coal are the long process, high investment, and relatively complicated operation. Because the price of coal is relatively low, the cost of hydrogen production is low. When the scale of hydrogen production is less than  $5 \times 10^4 \text{ Nm}^3 \cdot \text{h}^{-1}$ , the cost of hydrogen production from coal is high in the depreciation cost of fixed assets, which has no advantage compared with hydrogen production from natural gas. When the scale of hydrogen production is greater than  $5 \times 10^4 \text{ Nm}^3 \cdot \text{h}^{-1}$ , the depreciation cost of fixed assets in the cost of hydrogen production from coal is lower, and its hydrogen cost is competitive. The larger the scale of hydrogen production, the more obvious the cost advantage of the coal-to-hydrogen production route <sup>[19]</sup>.

**Coal accounts for 37% of the cost structure of hydrogen production from coal**



**Figure 1.14 Cost structure of hydrogen production from coal**

**Table 1.4 Comparison of the cost of hydrogen production from coal and hydrogen production from natural gas**

Item	Cost(Yuan·m <sup>-3</sup> )	
	Hydrogen production from natural gas	Coal to hydrogen
Raw material	0.988	0.387
Oxygen	--	0.21
Supplementary Materials	0.014	0.043
Fuel power consumption	0.184	0.069
Electricity	0.02	0.024
Recycled water	0.002	0.008
fresh water	0.001	0.001
Desalted water	0.022	0.036
3.5MP steam	-0.018	-
1.0MP steam	0	-
Fuel gas	0.157	-
Direct salary	0.012	0.012
Manufacturing costs	0.065	135
Financial and Management fees	0.029	0.06
Unit cost (Yuan·m <sup>-3</sup> )	1.42	0.92

Coal gasification hydrogen production technology has a history of more than one hundred years of development and can be divided into three generations of technologies: the first generation of technology is an atmospheric coal gasification process developed by Germany in the 1920s and 1930s. The typical processes include crushed coal and pressurized gasification. The fixed bed of the Lurgi furnace, the fluidized bed of the atmospheric Winkler furnace and the entrained bed of the atmospheric KT furnace, etc., these processes all use oxygen as the gasification agent, and implement continuous operation, and the gasification intensity and cold gas efficiency are greatly improved. The second-generation technology is a pressurized gasification process developed by Germany, the United States and other countries on the basis of the first-generation technology in the 1970s. Typical processes include Shell, Texaco, BGL, HTW, and KRW gasification processes. China's coal gasification hydrogen production process is mainly used for the production of synthetic ammonia. Over the years, a number of advanced coal gasification technologies with independent intellectual property rights have been developed, such as multi-nozzle coal-water slurry gasification technology, space furnace technology, and Tsinghua furnace technology. The third-generation technologies mainly include coal catalytic gasification, coal plasma gasification, coal solar gasification and coal nuclear waste heat gasification, which are still in the laboratory research stage.

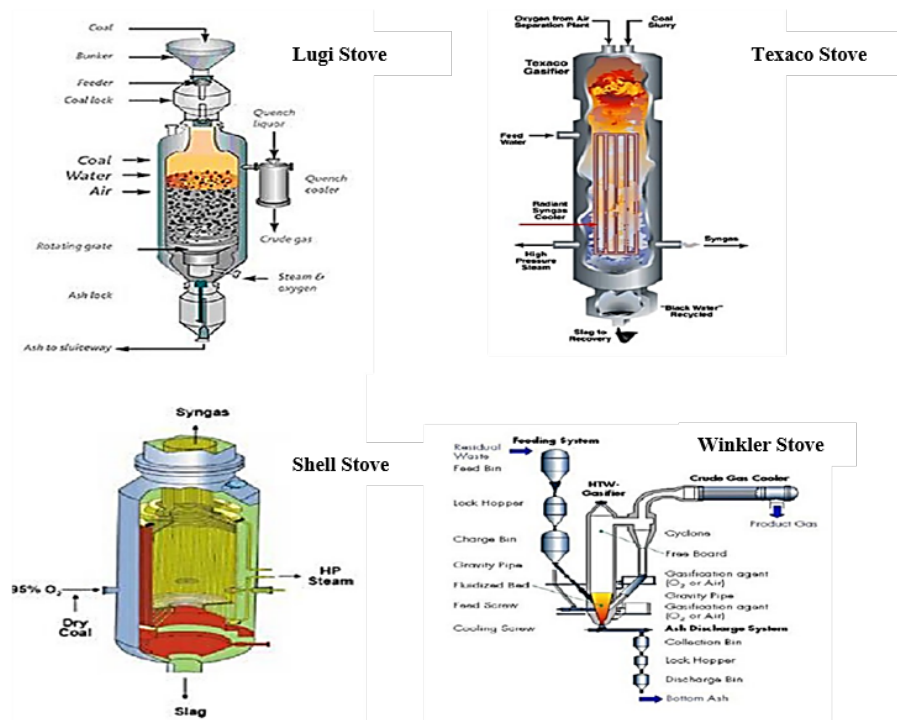


Figure 1.15 Schematic diagram of several typical coal gasifier structures [16]

In recent years, with the accelerated pace of China's refined oil quality upgrading, most new domestic refineries have chosen the full hydrogenation process route to meet the requirements of key technical and economic indicators such as light oil yield, product quality, and comprehensive commodity rate. According to preliminary statistics, there are 11 projects that have been determined to use coal to produce hydrogen (including petroleum coke) among the 15 projects under construction in China, including 20 million tons/year of Hengli Petrochemical Company,  $4.0 \times 10^7$  t/year of Zhejiang Petrochemical Company,  $2.6 \times 10^7$  t/year of Shenghong Petrochemical Company,  $2.0 \times 10^7$  t/year of Guangdong Petrochemical Company, China National Petroleum Corporation, and  $2.2 \times 10^7$  t/year of Huizhou Petrochemical Company, China National Petroleum Corporation,  $1.2 \times 10^7$  t/year of Yanshan Petrochemical Company, and  $1.8 \times 10^7$  t/year of Luoyang Petrochemical Company. Only the  $1.3 \times 10^7$  t/year oil refinery project of China National Petroleum Corporation Yunnan Petrochemical Company uses natural gas to produce hydrogen.

At present, China's largest coal-to-hydrogen company is the Shenhua Group, a subsidiary of China Energy Group. The group has built the world's first million-ton coal direct liquefaction demonstration plant. The plant uses two sets of SCGP

powder produced of Dutch Shell Company to provide hydrogen raw materials for coal liquefaction, hydrogenation stability, hydrogenation modification and other devices. A single set of daily hydrogen production capacity is 313 t, hydrogen purity is 99.5%,  $\text{CO} + \text{CO}_2 \leq 20 \mu\text{g} \cdot \text{g}^{-1}$ . At the same time, the company is also the largest hydrogen producer in China, with an annual hydrogen production of  $4.0 \times 10^4 \text{t}$ . On October 11, 2018, Zhuneng Group, a subsidiary of National Energy Group, signed the “*Framework Agreement for R & D Cooperation of Heavy Haul Mine Trucks with Hydrogen Energy above 200 tons*” with Hydrogen Technology Company, Beijing Low-Carbon Clean Energy Research Institute and Weichai Holding Group to jointly develop hydrogen-powered mining vehicles. This is after the passenger bus line, China’s hydrogen and fuel cell industry development in the field of transportation to take a new step<sup>[20]</sup>.

In addition, Professor Guo Liejin, academician of the Chinese Academy of Sciences and head of the State Key Laboratory of Multiphase Flow in Power Engineering, Xi’an Jiaotong University, led his scientific research team. After two decades of scientific research, a series of fully independent intellectual property technologies, known as “supercritical coal water gasification for hydrogen generation”, have been developed in 2016, successfully transforming coal chemical energy into hydrogen energy directly and efficiently, and eliminating the generation and emission of gaseous pollutants such as sulfide and nitride, and dust particles such as PM2.5 from the source. According to the calculations, if the technology is adopted in the thermal power industry in China,  $3.28 \times 10^8 \text{ t}$  of coal can be saved annually<sup>[21]</sup>. The team has successfully developed a series of experimental facilities including supercritical water fluidized beds, which can complete the complete vaporization of coal. Above  $700^\circ\text{C}$ , all kinds of domestic coal gasification rate reached 100 %. The integration and optimization of the thermodynamics and chemical reaction kinetic model and reaction system of supercritical water gasification hydrogen production have been completed. The pilot scale demonstration system with a processing coal volume of  $1 \text{ t} \cdot \text{h}^{-1}$  has been successfully completed. Through the technical and economic analysis, the price of hydrogen can be reduced to 0.7 yuan when the coal handling capacity of the system reaches  $8.33 \times 10 \text{ t} \cdot \text{h}^{-1}$ .<sup>[22]</sup>

How to improve the reaction rate of coal gasification to hydrogen efficiently has been a bottleneck restricting the development of coal gasification to hydrogen.

On the basis of previous studies, Shanxi Coal Chemistry Research Institute proposed to add alkali metal catalyst to promote the direct reaction rate of  $\text{Fe}_2\text{O}_3$  with coal. Adding  $\text{Al}_2\text{O}_3$ , on the one hand, as an inert component to prevent the sintering of iron oxide, on the other hand, it reacts with  $\text{FeO}$  to form an iron-aluminum-oxygen carrier, releasing reaction heat to provide part of the heat for the fuel reactor. The simulation results show that each reactor can realize self-heating during the process of adopting this technology, and the thermal efficiency of hydrogen production can reach 75%, and then the generated iron-aluminum oxygen carrier can be oxidized back to the initial phase state by air to realize oxygen cycle. Efficient and clean hydrogen production methods will be the direction of coal gasification development.

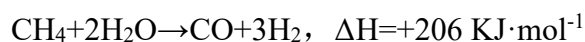
Due to China's the energy reserve structure of "more coal, less oil, and poor gas", the hydrogen production from coal will occupy an important position in the hydrogen production market for a long time. However, more cleaner processes and more energy-efficient network processes will become one of the research directions of this hydrogen production method. In addition, the high-efficiency catalysts and catalytic systems will also reduce the energy input of coal to hydrogen production, resulting in the greater economic and environmental benefits.

## 3.2 Hydrogen production from natural gas

### 3.2.1 Overview

Synthetic gas can be produced by reforming reaction or other reactions, and then  $\text{H}_2$  can be produced to reduce methane and  $\text{CO}_2$  emissions. China has rich natural gas reserves and good environmental acceptance. It is of dual significance for energy conservation and environmental protection. The hydrogen production from natural gas mainly includes natural gas reforming, partial oxidation reforming and catalytic cracking.

**Methane steam reforming** is currently the most mature technology and the most industrially used method. Its chemical reaction formula can be expressed as:



The reaction is a strong endothermic reaction, requiring additional heat



source, usually at high temperature above 800°C, the reaction pressure is 1.5-3.1 MPa. In addition to the formation of H<sub>2</sub>, the reaction also contains CO. There are two main types of catalysts used in the methane steam reforming process: non-noble metal catalysts (mainly Ni-based catalysts) and noble metal catalysts (such as Pt, etc), which are usually supported by MgO and Al<sub>2</sub>O<sub>3</sub>. Since methane steam reforming is the main way for industrial hydrogen production, a large number of catalysts must be used for hydrogen production. But the noble metal catalysts are rarely applied to the actual hydrogen production process due to their high cost, and the relatively inexpensive Ni-based catalysts are widely used in industrial hydrogen production. However, in addition to the main reaction, the Ni-based catalyst is also accompanied by a series of side reactions during the reaction process, and the carbon deposit formed by the decomposition of CO and CH<sub>4</sub> into solid carbon will cause the catalyst poisoning. In addition, high temperature is also easy to cause catalyst sintering and make the catalyst useless. In order to reduce the formation of carbon, avoid catalyst poisoning and lower catalyst activity, adding Mg, La, Ce and other elements to the catalyst can effectively inhibit the formation of carbon deposits and improve the activity of the catalyst. Methane steam reforming has been applied since 1926, which is currently the most mature technology and the most widely used method in industry. The conversion rate of methane can reach 85%, which is the highest conversion rate among natural gas reforming hydrogen production methods. Its disadvantages are high energy consumption, high production cost, expensive equipment, slow hydrogen production process and emissions of toxic gas CO and greenhouse gas CO<sub>2</sub> during the hydrogen production.

**Partial oxidation reforming.** Partial Oxidation of Methane has received extensive attention since the 1990s. Its chemical reaction formula is:



This reaction is a lightly exothermic without additional heat source or catalyst. The reaction pressure is atmospheric. In order to increase the conversion rate of methane and prevent the formation of particulate soot, the reaction temperature is usually up to 1300°C~1500°C. The high-temperature reactions are prone to produce solid carbon to form carbon deposits, and local high-temperature hot spots are prone to occur when the temperature is too high. The

generated heat brings great difficulties to thermal management. Usually, adding a catalyst can reduce the reaction temperature. The catalyst used in the partial oxidation reforming method is mainly a supported metal catalyst with metal components supported on a carrier. The metal components are usually Ni and Rh. However, these two catalysts will also bring about the problems of carbon deposition and high price. Krummecher et al. carried Rh on the carrier  $\text{Al}_2\text{O}_3$  and used it as a catalyst for the partial oxidation of methane to produce hydrogen. The reaction temperature was greater than  $800^\circ\text{C}$ , or even greater than  $1000^\circ\text{C}$ , which also needed to solve problems of thermal management and safety.

The partial oxidation reforming method is an exothermic reaction, which is faster than steam reforming. However, this method has a low conversion efficiency of 55 % ~ 65 %. The partial oxidation reforming method can utilize the heat generated by itself without external heating supply. However, the thermal management difficulties and safety problems caused by excessively high operating temperatures limit the development of partial oxidation reforming for hydrogen production.

**Autothermal catalytic reforming.** Autothermal Reforming of Methane (Autothermal Reforming of Methane) is to introduce steam in the partial oxidation reaction, generate heat in the partial oxidation reforming, absorb heat in the steam reforming, combines exothermic partial oxidation reforming with strong endothermic steam reforming, and controls exothermic and endothermic processes to achieve heat balance. The chemical reaction formula is:



In the reaction formula,  $0 < x < 1$ . There are two zones in the autothermal catalytic reforming reactor, one is the oxidation zone, where partial oxidation reforming takes place. The other zone is the catalytic zone, where steam reforming takes place. The oxidation catalyst is used in the oxidation zone, and the oxidation speed can be accelerated to quickly release heat, and the heat can provide the heat required for steam reforming in the catalytic zone.

In order to control the reaction temperature, avoid the formation of carbon deposits, while ensuring the hydrogen content in the product is as high as possible, in the whole process, the ratio of the amount of  $\text{O}_2$  and  $\text{CH}_4$  and the amount of  $\text{H}_2\text{O}$  and  $\text{CH}_4$  needs to be strictly and reasonable. With the increase of the molar

ratio of O<sub>2</sub> to CH<sub>4</sub> and the increase of oxygen content, the oxidation reaction can generate more heat, which is conducive to the progress of steam reforming. However, the ratio of O<sub>2</sub> and CH<sub>4</sub> substances is too large, the excessive oxygen content will lead to the deep oxidation of CH<sub>4</sub> to produce CO<sub>2</sub>, which will reduce the hydrogen production efficiency. Chan S H et al. calculated by simulation and calculated that the optimum value of the ratio of the amount of air-fuel substance is 3.5, and the optimum range of the ratio of the amount of steam to fuel substance is 2.5-4.0.

Autothermal catalytic reforming does not require an external heat source, which simplifies the system and reduces the start-up time. Compared with steam reforming, autothermal reforming starts and stops more quickly. Compared with partial oxidation reforming, the conversion efficiency of autothermal reforming to hydrogen methane is higher, with a conversion rate of 60% to 75%, which can produce more hydrogen. In addition, the structure of the autothermal reforming hydrogen production equipment is relatively compact, which makes this method of hydrogen production have good market potential. However, due to its high reaction temperature, its equipment needs high temperature resistance as part of the oxidation equipment, so the equipment cost is high.

**Catalytic cracking.** In recent years, the catalytic cracking of natural gas to hydrogen has been widely studied. The chemical reaction formula is:



The reaction is an endothermic reaction. The catalytic cracking of natural gas for hydrogen production is the catalytic decomposition of CH<sub>4</sub> at high temperature, which can not only obtain H<sub>2</sub> without CO and CO<sub>2</sub>, but also can obtain carbon nanotubes and carbon nanofibers. This method has received extensive attention in recent years.

The development of carbon-resistant catalysts is the key to the study of natural gas catalytic cracking for hydrogen production. The Ni/Zr catalyst and Ni/Cu catalyst prepared by the eutectic method by Ermakova and others have better carbon deposition resistance than the Ni and Ni/Cu catalyst made by the precipitation method. In addition, the type of catalyst support also has an impact on the catalytic cracking of methane. Zhang Zhi et al. prepared Ni/MgO and Ni/OD (diamond oxide) catalysts by impregnation. The catalytic activity is

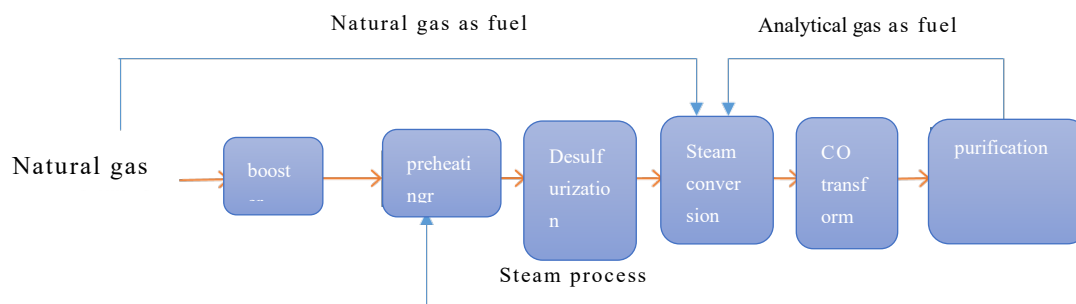
maintained for a long time at 500 – 600°C, but the conversion efficiency of the 41Ni/MgO catalyst is higher than that of the 33Ni/OD catalyst. The methane conversion rate of the former can reach 25% within 120 minutes, while the methane conversion rate of the latter is only 8% within 150 minutes. Takenaka et al. loaded Ni on SiO<sub>2</sub>, TiO<sub>2</sub>, C (graphite), ZrO<sub>2</sub>, MgO, MgO-SiO, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> to study its activity and life, and found that Ni/SiO<sub>2</sub>, Ni/C and Ni/TiO<sub>2</sub>. The methane cracking conversion rate of TiO<sub>2</sub> catalyst is higher than that of other catalysts, and the life of Ni/ SiO<sub>2</sub> is the longest, while Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/MgO- SiO<sub>2</sub>, Ni/MgO lose their activity soon after contact with methane. Choudhary et al. carried Ni on the carrier HZSM-5, HY, activated carbon, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and conducted research and found that 65% Ni/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>, 10% Ni/SiO<sub>2</sub>, 10% Ni/HY catalyst can be maintained within 8 h High catalytic activity, while Ni/HZSM-5 and Ni/C catalysts gradually lose their catalytic activity from the beginning. The transmission electron microscope (TEM) test shows that carbon is filamentous on 65% Ni/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>, 10% Ni/SiO<sub>2</sub>, 10% Ni/HY, forming carbon nanomaterials, which can maintain good activity, while carbon On Ni/HZSM-5, it is hermetically distributed, thus deactivating the catalyst. In addition to metal catalysts, certain non-metal catalysts also have catalytic effects on cracking, such as activated carbon, graphite, carbon black, and nanostructured carbon. Muradov studied the use of activated carbon, carbon black, and nanostructured carbon as catalysts to crack methane to produce hydrogen. The results found that methane cracking on various activated carbons has higher initial activity. As the reaction proceeds, the methane conversion rate will gradually reduce to a stable state. The initial activity of methane cracking on carbon black is related to the specific surface area of carbon black. The larger the specific surface area of carbon black is, the higher the initial activity is. The initial activity of methane on nanostructured carbon is relatively low, about 1/10 of activated carbon.

Catalytic cracking is used to generate carbon and high-purity hydrogen from methane without producing carbon oxides, and no further shift reaction is required to remove carbon oxides to purify hydrogen. Its production equipment is simpler than other natural gas reforming, which can shorten the process and reduce investment. Therefore, this method has broad market prospects for hydrogen production. However, the carbon produced by this method has specific

uses and markets. If the large amount of by-product carbon produced cannot good use will limit the development of this technology.

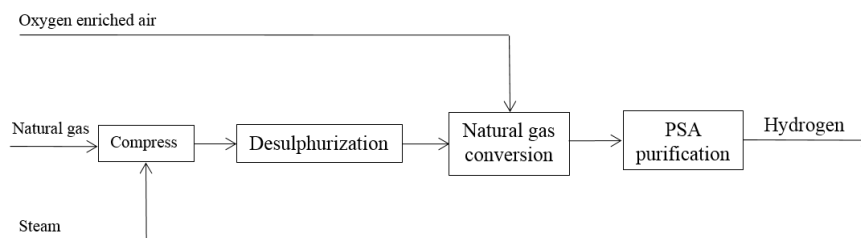
### **3.2.2 Principle and process**

The typical process of methane steam reforming and partial oxidation hydrogen production is shown in Figure 1.16. The early methane steam reforming process was carried out under normal pressure, but the thermal efficiency and equipment production capacity can be improved by increasing the reaction pressure. The specific process includes feed gas pretreatment, steam reforming, CO shifting and hydrogen purification. The mass fraction of hydrogen in the product is greater than 99.99%, which meets the hydrogen purity requirements of hydrogen fuel cell vehicles. The pressure of the product is about 1.6 MPa, and it needs to be filled to 20 MPa and transported to the hydrogen refueling station by tanker<sup>[23]</sup>.



**Figure 1.16 Methane steam reforming hydrogen production process** <sup>[17]</sup>

Figure 1.17 shows the typical process flow of partial oxidation of natural gas to hydrogen. After the natural gas is compressed and desulfurized, it is mixed with steam and preheated to about 500°C, and then mixed with oxygen or oxygen-enriched air (also preheated to about 500°C) into the reactor from the top of the reactor in two streams for partial oxidation reaction. The lower part of the reactor emits reforming gas, the temperature is 900~1000°C, the hydrogen content is 50%~60%. This process uses the heat in the reactor to carry out the hydrocarbon steam reforming reaction, so it can widely select hydrocarbon raw materials and allow more impurities to exist (the conversion of heavy oil and residual oil mostly uses partial oxidation), but it needs to be equipped with an air separation device or a variable The investment of pressure adsorption oxygen generator is higher than that of natural gas steam reforming method. The reactor for hydrogen production by partial oxidation of natural gas uses high-temperature inorganic ceramic oxygen permeable membranes, which can separate pure oxygen from the air at high temperatures and prevent nitrogen from entering the synthesis gas. Compared with traditional steam reforming, the energy consumption of the process is significantly lower consumption, which can reduce investment costs to a certain extent <sup>[24]</sup>.



**Figure 1.17 Typical process flow diagram of partial oxidation of natural gas to hydrogen production** <sup>[17]</sup>

### 3.2.3 Development status

For hydrogen production from natural gas, the overall cost of hydrogen is related to the annual operation time of the project and the price of natural gas. Relevant studies have shown that the same natural gas price, the total operating time reduced from 8,000 hours to 3200 hours, the comprehensive cost of hydrogen increases by about  $0.83 \text{ yuan} \cdot \text{m}^{-3}$ . In addition, under the same annual operating time, the price of natural gas increased from  $2.0 \text{ yuan} \cdot \text{m}^{-3}$  to  $4.0 \text{ yuan} \cdot \text{m}^{-3}$ , and the production cost of hydrogen increased by about  $1.02 \text{ yuan} \cdot \text{m}^{-3}$  [25].

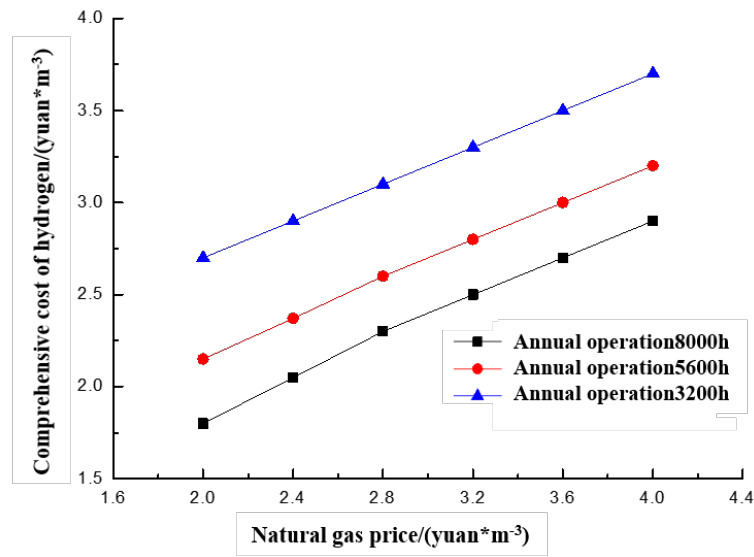


Figure 1.18 The influence of natural gas price and annual operating time on the comprehensive cost of hydrogen [25]

Specific to a certain natural gas hydrogen production enterprise, the cost of natural gas hydrogen production mainly includes two aspects: one is variable cost, one is variable cost, this variable cost mainly refers to electricity, cooling water costs, deionized water costs, etc., two is the immutable cost, which mainly includes maintenance fees, office expenses, wages, etc. The proportion of these two parts is also related to production capacity. Table 1.5 compares the proportions of variable and non-variable costs when the production capacity is  $1.0 \times 10^3$  and  $1.0 \times 10^4 \text{ m}^3$  of hydrogen per year. Therefore, if the benefits of hydrogen production from natural gas are to be maintained, a certain production scale is essential.

**Table 1.5 The proportions of variable costs and immutable costs under different production capacities**

produce 1 m <sup>3</sup> hydrogen	Variable costs					Immutable cost		
	Deionized water	Cooling water	Electricity bill	Gas cost	Depreciation	Maintenance fees	Employee salary	Marketing fee and management fee
Annual production capacity 1.0×10 <sup>4</sup> m <sup>3</sup> hydrogen	3.42%	0.73%	9.97%	79.73%	0.18%	0.24%	0.09%	5.63%
Annual production capacity 1.0×10 <sup>3</sup> m <sup>3</sup> hydrogen	2.69%	0.58%	7.85%	62.80%	14.24%	0.19%	7.22%	4.44%

As mentioned in the section on hydrogen production from coal, as two important industrial hydrogen production methods, the comparison between hydrogen production from natural gas and hydrogen production from coal is of great significance. The corresponding relationship between hydrogen production from natural gas and hydrogen production from coal at the same cost is shown in Figure 1.18. It can be seen from the figure that when the price of natural gas is 1.67 yuan·m<sup>3</sup> and the price of coal is 450 yuan·t<sup>-1</sup>, the hydrogen cost of hydrogen production from natural gas and coal to hydrogen production is 0.87 yuan·m<sup>3</sup>; the price of natural gas is 2.52 yuan·m<sup>-3</sup>. When the price of coal rises to 850 yuan·t<sup>-1</sup>, the cost of hydrogen produced is 1.15 yuan·m<sup>-3</sup> [26].

**Table 1.6 Schematic diagram of the correspondence relationship between the same cost of hydrogen production from natural gas and hydrogen production from coal**

Hydrogen (standard state) cost / (Yuan·m <sup>-3</sup> )	Natural gas (standard state) price / (Yuan·m <sup>-3</sup> )	Coal price / (Yuan·t <sup>-1</sup> )
0.87	1.67	450
0.94	1.88	550
1.01	2.10	650
1.08	2.31	740
1.15	2.52	850
1.22	2.74	950

Although the current hydrogen production from natural gas has the dual significance of energy saving and environmental protection, it is undeniable that there



are still many problems. These include: (1) The economic benefits are relatively poor, the cost of the traditional hydrogen production industry is too high, and the cost of fuel is too high. (2) The waste heat collection and reuse are not high, and the flue outlet temperature is too high in the hydrogen production process, resulting in a lot of heat waste. (3) Hydrogen production requires high-temperature reactions, the equipment is relatively expensive, and a large amount of fuel gas is required, which makes the cost of hydrogen production too high. (4) A large amount of carbon dioxide will be left in the process of hydrogen production, which will not only waste resources, but will even cause excessive carbon dioxide to directly affect the environment. High efficiency and low energy consumption have become a general trend in the development of natural gas hydrogen production. Large-scale equipment and stable technology have placed higher requirements on the factory. At present, there is still a big gap between China and the international level in key equipment such as large-scale reformers and their key supporting equipment, large-scale compressors, large-scale PSA equipment, and efficient and durable catalysts. In order to narrow this gap, our country's hydrogen production companies should develop the following aspects: (1) develop corresponding supporting facilities and technological processes; (2) vigorously develop the level of science and technology, and increase the utilization rate of catalysts; (3) need to increase the use of other precious metals Catalyst research level; (4) Increase investment in hardware facilities, and better provide large-scale chemical furnaces and related equipment <sup>[27]</sup>.

The future development direction of hydrogen production from natural gas <sup>[27]</sup>: (1) Hightemperature cracking hydrogen production technology. The pyrolysis of natural gas for hydrogen production is the catalytic decomposition of natural gas into hydrogen and carbon at high temperature. This process is considered to be a transition process between fossil fuels and renewable energy because it does not produce carbon dioxide. Liaohe Oilfield has carried out extensive research work on the hightemperature catalytic cracking of natural gas to produce hydrogen. The carbon produced can have specific important uses and broad market prospects. (2) Hydrogen production by autothermal reforming. This process has changed from external heating to internal self-provided heat source, which is more reasonable for energy utilization. This process is mainly because the heat generated by the reaction can be used by other reactions that require heat

to realize self-heating. The working principle of this technology is to couple some heat in the reactor. The heat is mainly produced by the combustion reaction of natural gas. At the same time, the natural gas can be reacted with water vapor to realize the self-heating of the reaction. In addition, since the strong exothermic reaction and strong endothermic reaction in the thermal reforming reactor are carried out step by step, this process still requires some high-end high-temperature resistant instruments, which also increases the cost of hydrogen production from natural gas, and also has disadvantages such as low productivity.

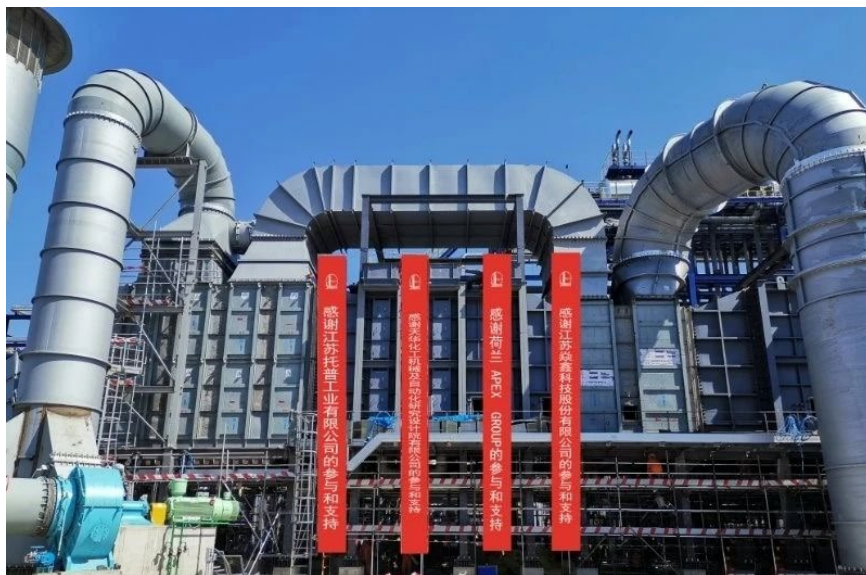
(3) Hydrogen production technology by adiabatic conversion. Adiabatic conversion hydrogen production technology is currently relatively advanced. The biggest feature of this technology is that its reaction is a partial oxidation reaction, which can improve the capacity of the natural gas hydrogen production device and better control the reaction speed and operation steps. The natural gas conversion hydrogen production process mainly uses air oxygen source. The designed reactor with oxygen distributor can solve the hot spot problem of the catalyst bed and the reasonable distribution of energy. The reaction stability of the catalytic material is also better due to the reduction of the hot spot. Greatly improved. The new process has the advantages of short process flow and simple operation unit. Through this process, investment costs and hydrogen production costs can be reduced, and the economic benefits of enterprises can be improved.

(4) Technology of hydrogen production by partial oxidation of natural gas. Compared with the traditional steam reforming method, the natural gas oxidation hydrogen production technology has lower energy consumption. It mainly uses relatively inexpensive refractory materials for stacking reaction, but this process also requires relatively high purity oxygen, which also increases the cost of oxygen production and equipment.

(5) Value analysis of hydrogen production process from natural gas. As a chemical product, hydrogen is widely used in production and life, not only in light industry but also in heavy industry. With the development of new energy technology and the increase of people's awareness of environmental protection, hydrogen is used as a renewable resource. It is widely used in production and life, such as medicine, electronics, electrical, fine chemicals and many other industries.

Currently, hydrogen production from natural gas is mainly still in the

development of equipment. In June 2020, the  $1.0 \times 10^4 \text{ Nm}^3 \cdot \text{h}^{-1}$  natural gas hydrogen conversion gas steam generator (waste heat boiler) designed and supplied by Tianhua Chemical Machinery and Automation Research and Design Institute for Sinopec Tianjin Branch was installed on site, and the whole hydrogen production unit was delivered (Figure 1.19) [28].



**Figure 1.19  $1.0 \times 10^4 \text{ Nm}^3 \cdot \text{h}^{-1}$  Natural Gas Hydrogen Production Plant of Sinopec Tianjin Branch**

The  $100,000 \text{ Nm}^3 \cdot \text{h}^{-1}$  natural gas hydrogen production plant is a single set of large-scale hydrogen production plant that adopts domestic technology (process package) nationwide and is designed by a domestic design institute (technical design is purely domestic). Among them, the converter gas steam generator is one of the key core equipment that plays a role in heat recovery and energy saving, and the domestic technology research and design institute of Tianhua Chemical Machinery and Automation is responsible for it. The successful delivery of  $1.0 \times 10^4 \text{ Nm}^3 \cdot \text{h}^{-1}$  natural gas hydrogen conversion gas steam generator will further promote the localization of the whole hydrogen production device, and form a complete set of waste heat equipment technology with independent intellectual property rights with thin tube plate steam generator as the core, which makes important contributions to energy saving, consumption reduction and emission reduction. The market promotion prospect is broad, which is of great significance to the development of China's hydrogen production industry and national hydrogen energy security.

### 3.3 Hydrogen production from alcohols (methanol, ethanol)

#### 3.3.1 Overview

Alcohol hydrogen production mainly includes methanol and ethanol. The most widely used technology is methanol hydrogen production. There are three ways to produce hydrogen from methanol: methanol decomposition, methanol partial oxidation and methanol steam reforming (Fig.25). Hydrogen production from methanol steam reforming is more widely used because of high hydrogen yield (the hydrogen composition of the product can be close to 75% from the reaction formula), reasonable energy utilization, simple process control and convenient industrial operation. Methanol and desalted water are mixed in a certain proportion preheated by the heat exchanger and feed into the vaporization tower. The vaporized methanol water vapor is superheated by the superheater and then enter into the tubular reactor. Methanol and water vapor are reformed at 200°C~300°C, 1 MPa~2 MPa and catalyst to produce H<sub>2</sub>, CO<sub>2</sub> and a small amount of CO. The mixed gas enters the water washing absorption tower after heat exchange and cooling. The unconverted methanol and water are collected in the tower kettle for recycling and utilization, and the tower top gas is sent to the pressure swing adsorption device for purification [29].

Based on the characteristics of methanol hydrogen production technology, hydrogen can be produced in the station, and it is now used without the need for large-scale transportation and storage of H<sub>2</sub>. It can also be concentrated in the chemical industry park to produce hydrogen, and then transported to the hydrogenation station through short distance (<100 km). The two application methods are feasible. With the breakthrough of CO<sub>2</sub> methanol synthesis technology, methanol hydrogen production can further develop into methanol hydrogen storage, so as to achieve zero emission of CO<sub>2</sub>, showing a broader application prospect.

**Table 1.7 Technical methods and comparison of hydrogen production from methanol** [30]

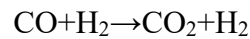
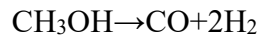
Technical method	Reaction	Technology maturity	Large-scale application
Methanol cracking	$\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2$	mature	For synthesis gas preparation

Methanol steam reforming	$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$	mature	For hydrogen production, the largest scale $60000\text{Nm}^3 \cdot \text{h}^{-1}$
Partial oxidation of methanol	$\text{CH}_3\text{OH} + 0.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$	in development	-

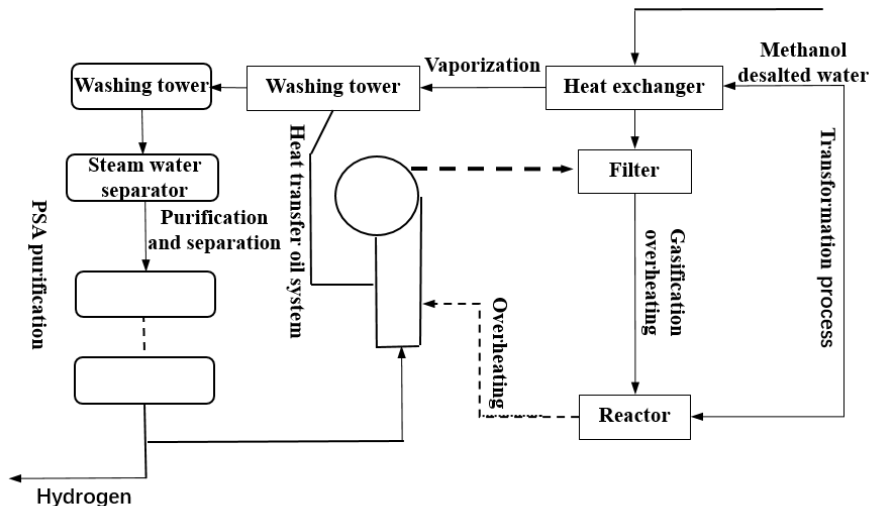
### 3.3.2 Principle and process

The reaction mechanism of hydrogen production from methanol steam reforming is mainly divided into decomposition-transformation mechanism and reforming-inverse transformation mechanism <sup>[31]</sup>.

Decomposition-transformation mechanism: In the hydrogen production reaction of methanol steam reforming, methanol decomposition reaction first occurs to generate CO and H<sub>2</sub>, and then transformation reaction occurs to generate CO<sub>2</sub>. The reaction mechanism is as follows:



Reforming-inverse conversion mechanism: In the process of hydrogen production from methanol steam reforming, methanol reforming reaction firstly generates CO<sub>2</sub> and H<sub>2</sub>, and then reverse conversion reaction generates CO. Methanol has the advantages of high energy density, wide source, safe and reliable. At present, the methanol reforming has become the most widely used and mature technology for hydrogen production due to its low reaction temperature, low cost and high hydrogen production rate. However, due to the trace amount of CO in the product of methanol reforming hydrogen production, it will poison the precious metal catalyst, resulting in a sharp decline in performance. Because the structure of microchannel reaction directly affects the effect of methanol reforming to hydrogen, so scholars at home and abroad have also studied the microchannel reactors with different structure forms, in order to optimize the flow field and improve the reaction efficiency. It is an important direction for future research to explore and study the new and efficient microchannel structure and the matching of catalysts <sup>[32]</sup>. The typical methanol reforming process is shown in Figure1.20.



**Figure 1.20 Typical process flow of methanol reforming hydrogen production and pressure swing adsorption [33]**

Methanol and desalinated water are mixed in a certain proportion and then preheated by the heat exchanger and sent to the vaporization tower. The vaporized water methanol steam is superheated by the heat exchanger and then enters the converter. The catalyst bed is subjected to catalytic cracking and shift reaction to produce conversion. The gas contains about 74% hydrogen and 24% carbon dioxide. After heat exchange, cooling and condensation, it enters the washing absorption tower. The tower still collects unconverted methanol and water for recycling, and the tower item gas is sent to a pressure swing adsorption device for purification. According to the different requirements of product gas purity and trace impurity components, the purity can reach 99.9~99.999% by using four or more towers. A pressure swing adsorption device with a designed processing capacity of  $1.5 \times 10^3 \text{ Nm}^3 \cdot \text{h}^{-1}$  reformed gas and a purity of 99.9% has a hydrogen recovery rate of over 90%. The carbon dioxide in the converted gas can be purified to food grade with a pressure swing adsorption device for use in the beverage and wine industries. This can greatly reduce production costs. The process is set up after the separation of carbon dioxide by pressure swing adsorption device, the hydrogen rich conversion gas is pressurized into the pressure swing adsorption device to purify<sup>[34]</sup>.

### 3.3.3 Development status

Methanol hydrogen production has some instinctive advantages: (1) From

the aspect of raw material supply, the raw material of methanol hydrogen production technology is  $\text{CH}_3\text{OH}$ , which is an important coal chemical product and organic chemical raw material. Relevant data show that the effective production capacity of China's  $\text{CH}_3\text{OH}$  in 2017 was approximately  $7.644 \times 10^7 \text{t}$ .  $\text{CH}_3\text{OH}$  can also be obtained from the conversion of natural gas, biomass, etc., in particular, it can be produced from  $\text{CO}_2$  by using new energy sources such as solar energy and wind energy to truly realize the sustainable production of  $\text{CH}_3\text{OH}$ . In addition,  $\text{CH}_3\text{OH}$  is a liquid, belonging to bulk chemicals, transportation and storage technology is mature and convenient. (2) Strong technical and economical. This technology has been used in industry for many years, there are no technical problems, and it has good economic efficiency. At present, the production cost of coal-based methanol is  $1,000 \text{ yuan} \cdot \text{t}^{-1}$  to  $1,500 \text{ yuan} \cdot \text{t}^{-1}$ , and at the market price of  $2,500 \text{ yuan} \cdot \text{t}^{-1}$  to  $3,000 \text{ yuan} \cdot \text{t}^{-1}$ , the production of 1 kg of  $\text{H}_2$  consumes 6 kg of  $\text{CH}_3\text{OH}$ , plus other production costs (including equipment investment and depreciation, personnel costs, operating costs, etc.), the total cost of hydrogen production is  $25 \text{ yuan} \cdot \text{kg}^{-1}$  to  $30 \text{ yuan} \cdot \text{kg}^{-1}$ .

According to the investigation, most of the hydrogen production from methanol reforming is self-produced and sold by chemical plants, which is used to further improve the quality of deep hydrodesulfurization of oil products. Hydrogen is rarely used as a product for external sales and profit. Methanol to hydrogen is easy to produce and sell itself in chemical plants. The main reason is flexibility: (1) The investment of methanol to hydrogen plant is low and the construction period is short. Due to the simple process, the investment and construction cycle of methanol hydrogen production plant is much lower than that of coal gasification and natural gas reforming. (2) The methanol hydrogen production unit is flexible in scale and easy to obtain raw materials. Similarly, due to the short process of methanol cracking hydrogen production, the cost of methanol hydrogen production has little change under different device sizes, so the device size can be flexibly designed according to hydrogen demand. Coal to hydrogen is only suitable for large-scale hydrogen demand. (3) Methanol hydrogen project approval is easy. In the increasingly stringent environmental requirements of the moment, compared with other hydrogen production routes, methanol hydrogen project approval is easier. Taking the ten methanol hydrogen

production projects completed and under construction in Shandong Province from 2016 to 2017 as examples (table 1.8).

**Table 1.8 2016-2017 Methanol Hydrogen Production Projects in Shandong Region** <sup>[35]</sup>

Company Name	Hydrogen demand	Methanol to hydrogen ( $\text{Nm}^3 \cdot \text{h}^{-1}$ )	Methanol consumption ( $\times 10^4/\text{Year}$ )
Shandong Shengqi Chemical	Heavy oil refining	40000	16.96
Shandong Haike Chemical Industry	Oil quality upgrade	20000	8.48
Shandong Binhua Binyang Burning Chemical	Diesel upgrading	30000	12.72
Shandong Jincheng Petrochemical	Oil quality upgrade	60000	25.44
Shandong Red Sea Chemical	Oil product reform	15000	6.36
Shandong Shenchu Chemical	Residue desulfurization	40000	16.96
Shandong Dongfang Hualong Industry and Trade	Oil quality upgrade	60000	25.44
Dongying Qirun Chemical	Oil quality upgrade	30000	12.72
Guangrao Kelida Petrochemical	Oil quality upgrade	25000	10.6
Binzhou Federal New Energy	Light oil refining	1500	0.636
Total		321500	136.316

The above-mentioned ten largest methanol hydrogen production plants have a total hydrogen production scale of  $3.215 \times 10^5 \text{ Nm}^3 \cdot \text{h}^{-1}$ , and methanol demand will reach  $1.36 \times 10^6/\text{year}$ . Methanol to hydrogen, together with methanol to olefins (MTO), will become the most promising component of methanol demand structure in China <sup>[35]</sup>.

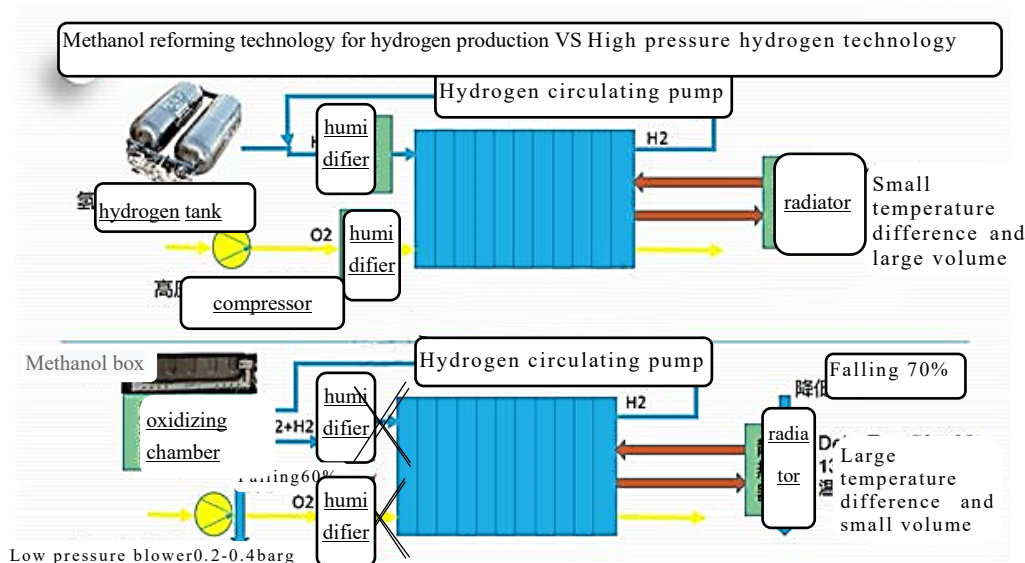
In terms of equipment supply, Changzhou Lanbo Purification Technology Co., Ltd. has the ability to provide complete sets of methanol reforming equipment. The equipment provided by the company can produce hydrogen from methanol up to  $2.0 \times 10^4 \text{ Nm}^3 \cdot \text{h}^{-1}$ . The purity of hydrogen produced by this equipment can reach 99.9-99.9999%, in which the concentration of carbon dioxide  $\text{CO}_2$  is  $\leq 5 \text{ ppm}$ , and the concentration of carbon monoxide  $\text{CO}$  is  $\leq 5 \text{ ppm}$  (Figure 1.21).



Methanol is currently the best material for hydrogen production, but the reason that restricts the development of hydrogen energy is the high cost of storage and transportation. Hydrogen energy is the molecule with the smallest volumetric energy density and is the easiest to leak. The cost of hydrogen production is very low, but the cost of storage is high. Therefore, many companies and scientific research units are now studying online hydrogen production from methanol. Shanghai Bo Hydrogen New Energy Technology Co., Ltd., on the basis of in-situ methanol reforming to produce hydrogen, deletes equipment such as hydrogen circulation pumps and air pumps, and directly burns and utilizes on the basis of in-situ methanol hydrogen production. And drive the engine to run, which can be used as a good source of power. Figure 1.22 shows the comparison between this new technology and the previous technology route.



Figure 1.21 Methanol reforming hydrogen production equipment of Changzhou Lanbo Purification Technology Co., Ltd. <sup>[33]</sup>



**Figure 1.22 The in-situ utilization of methanol reforming hydrogen production can reduce equipment schematic diagram** <sup>[36]</sup>

As far as the development direction is concerned, taking methanol to hydrogen as the hydrogen source of hydrogenation station, whether it is to adopt distributed hydrogen production or centralized hydrogen production in chemical industry park, its advantages are obvious and feasible. However, compared with the current fuel vehicle, the hydrogen fuel cell vehicle with methanol to hydrogen technology can reduce CO<sub>2</sub> emissions, but it does not completely solve the problem of carbon emissions, there is still room for improvement and development. The methanol-to-hydrogen process can be developed into a methanol-to-hydrogen storage process, which uses CH<sub>3</sub>OH as the hydrogen storage molecule and provides H<sub>2</sub> for the hydrogenation station through methanol-to-hydrogen. At the same time, the CO<sub>2</sub> emitted from the hydrogen production process is recycled and reused, and CH<sub>3</sub>OH is synthesized by catalytic hydrogenation or photoelectrocatalysis, forming a closed-loop process to achieve zero emission of CO<sub>2</sub>.

There are a lot of research on the technology of CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH at home and abroad. The team of Zhao Ning researcher of Shanxi Coal Chemical Institute of Chinese Academy of Sciences has carried out in-depth research on copper-based catalysts. The copper-based catalysts have been scaled up and industrial single-tube experiments have been carried out. At present, the design of 1.0×10<sup>5</sup> t process package is being carried out. The solid solution ZnO-ZrO<sub>2</sub> catalyst which developed by Li Can, Dalian Institute of Chemicals, Chinese

Academy of Sciences, it shows excellent catalytic performance for CO<sub>2</sub> hydrogenation and runs continuously for 500 hours without deactivation.

At the 24th Lanzhou Investment and Trade Negotiation in July 2018, the Dalian Chemical Institute of the Chinese Academy of Sciences, together with Lanzhou New Area Petrochemical Industry Group Co., Ltd. and Suzhou Gaomai New Energy Co., Ltd., signed a cooperation agreement on the development project of 1000 tons of carbon dioxide hydrogenation to methanol, with the goal of establishing an industrial demonstration project for 1000 tons of carbon dioxide hydrogenation to methanol.

Foreign development is faster, there have been industrial demonstration plants in operation, such as Norway Iceland 4.0×10<sup>3</sup>t/year demonstration plant. Especially with the development of renewable energy technologies such as solar energy and wind energy, the photoelectrocatalytic synthesis of CH<sub>3</sub>OH using CO<sub>2</sub> and H<sub>2</sub>O as raw materials is more attractive, so as to truly realize the good wishes of mankind. It can be expected that with the innovation and development of carbon dioxide synthesis of methanol technology, it is bound to achieve industrialization. Therefore, the application of CH<sub>3</sub>OH as hydrogen storage molecule in hydrogen fuel cell vehicles to achieve zero emission of CO<sub>2</sub> has broad application prospects.

With the rapid development of hydrogen fuel cell vehicle industry, the layout and construction speed of hydrogenation stations will be bound to accelerate. Methanol to hydrogen as hydrogen source of hydrogenation station, its raw material source and hydrogen production technology have a solid guarantee, good application economy, and energy saving and emission reduction effect is obvious. Methanol to hydrogen can provide hydrogen source for hydrogenation station through two application methods of hydrogen supply in station and hydrogen supply outside station. Among them, hydrogen production in station is now available without large amount of transportation and storage of H<sub>2</sub>, which has more advantages. In addition, with the continuous progress of scientific research, methanol to hydrogen can be further developed into methanol hydrogen storage, so as to achieve zero emission of CO<sub>2</sub>, which has a broader application prospect. In short, the application of methanol-to-hydrogen technology as the hydrogen source of hydrogenation station in the hydrogen fuel cell industry has practical

feasibility and broad development prospects <sup>[30]</sup>.

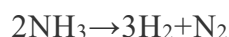
## **3.4 Liquid Ammonia Hydrogen Production**

### **3.4.1 Overview**

With liquid ammonia as raw material, the hydrogen-nitrogen mixed gas containing 75% hydrogen and 25% nitrogen is obtained by heating decomposition under the action of catalyst. The ammonia decomposition gas generator has the characteristics of simple structure, low investment and high efficiency. At present, many catalysts can effectively crack ammonia to release hydrogen, but the best catalyst is still precious metals. In fact, the manufacturing cost of ammonia is very low, and ammonia can also be stored in a suitable plastic tank at low pressure and then put on the car. In addition, the construction of ammonia stations is also as simple and convenient as the construction of liquefied petroleum gas (LPG) stations. Therefore, the latest research is expected to vigorously accelerate the pace of hydrogen as a green fuel for transportation.

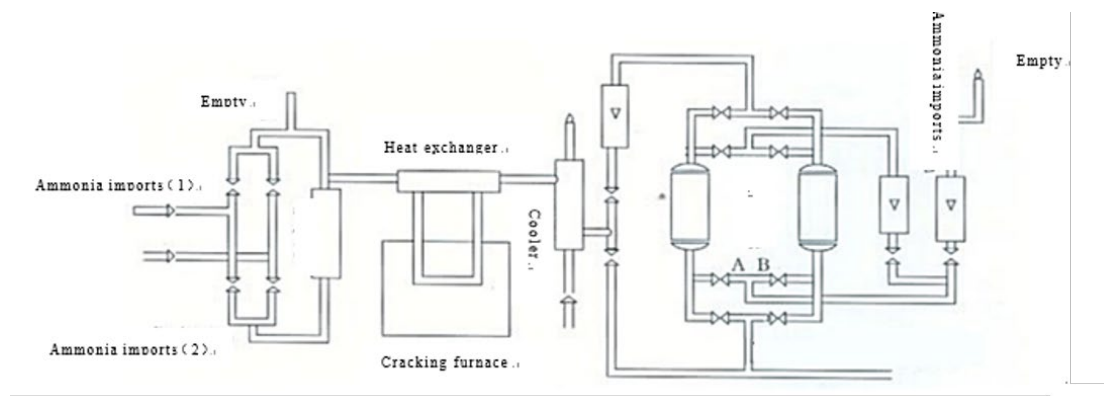
### **3.4.2 Principle and process**

Ammonia (gaseous) is cracked into 75% hydrogen and 25% nitrogen under the action of a catalyst at a certain temperature. The main reactions are:



Because the whole process is an endothermic expansion reaction, increasing the temperature is conducive to ammonia cracking, and at the same time it is a volume expansion reaction, and reducing the pressure is conducive to ammonia decomposition.

Hydrogen production from ammonia decomposition using liquid ammonia as the raw material, the ammonia is heated to a certain temperature in ammonia decomposition furnace (cracking furnace) after gasification. Under the action of catalyst, ammonia is decomposed to produce a mixture of hydrogen (75 %) and nitrogen (25 %). The gas is purified by heat exchanger and cooler, and then used by molecular sieve adsorption purification device. The typical process is shown in Figure 1.23. The advantages are that the raw material ammonia is easy to obtain, the price is low, and the raw material consumption is small. Ammonia pyrolysis



**Figure 1.23 Process flow of hydrogen production by decomposition of liquid ammonia <sup>[37]</sup>**

Ammonia cracking hydrogen production furnace can be used for bright annealing of non-ferrous metals, silicon steel, chromium steel and stainless steel and other metal materials and parts, decarburization treatment of silicon steel sheets, copper-based, iron-based powder metallurgy sintering, and hydrogen-burning treatment of metal parts of electric vacuum devices, Protection sintering and sealing of semiconductor devices, palladium alloy membrane diffusion and purification of hydrogen raw material gas, etc. [38].

### 3.4.3 Development status

At present, the scale and device of hydrogen production from ammonia decomposition are relatively small, and there is no large-scale device for industrialization. In terms of the production of ammonia decomposition hydrogen production equipment, Suzhou Shouxing Purification Equipment Manufacturing Co., Ltd. has a good industry accumulation. The ammonia decomposition hydrogen production device uses liquid ammonia (purity $\geq$ 99.8%) as raw material to vaporize liquid ammonia into ammonia into the decomposition furnace body. At high temperature, ammonia is cracked to 75% hydrogen and 25% nitrogen under the action of nickel catalyst. The gas production of the device is 5~800 Nm<sup>3</sup> (adjustable), the product gas composition is 75% H<sub>2</sub> and 25% N<sub>2</sub> mixture, the product gas pressure is 0.05 MPa, the residual ammonia content is less than 10 ppm, and the product gas oxygen content is less than 3 ppm. In addition, Suzhou Nat Cloud Purification Equipment Co., Ltd. also has rich experience in

manufacturing ammonia decomposition hydrogen production equipment.



**Figure 1.24 Suzhou Shouxing Purification Equipment Manufacturing Co., Ltd. Liquid ammonia decomposition hydrogen production device <sup>[39]</sup>**

At present, most of the hydrogen production from liquid ammonia is focused on the upgrading of catalysts. At present, the commercial catalyst is Cu-Ni-Al<sub>2</sub>O<sub>3</sub> and some additives are added. Ammonia decomposition technology coupled with other processes (such as light) has become the future research direction. A paper published by Rice Laboratory of Nanophotonics (LANP) in “*Science*” magazine described new catalytic nanoparticles, which are mainly made of copper and trace ruthenium metal. The test results show that the catalyst can catalyze the photo-induced electrochemical process, which significantly reduces the activation barrier of photo-decomposition of ammonia molecules to produce hydrogen and nitrogen. This process begins with the adhesion or adsorption of ammonia on ruthenium, and a series of steps are carried out as the bond in ammonia is broken one by one. The remaining hydrogen and nitrogen atoms combine with another hydrogen and nitrogen atoms to form hydrogen and nitrogen, and then leave or desorb from the ruthenium surface. Because nitrogen has strong affinity and adhesion to ruthenium, it prevents the surface from attracting other ammonia molecules. To drive it away, more energy must be added to the system.

The efficiency of LANP copper-ruthenium catalyst comes from the light-induced electronic process, which produces local energy at the ruthenium reaction

site, which contributes to the desorption. This process, known as the “thermal carrier-driven photocatalytic effect”, originates from the continuous rotation of the electron sea through copper nanoparticles. Some wavelengths of the incident light resonate with the electron sea, and a rhythmic oscillation called local surface plasmon resonance is established. Plasmas can be used to increase the number of transient high-energy electrons called “hot carriers” hitting metals. Plasma nanoparticles can be combined with catalysts in the “antenna reactor” design. Plasma nanoparticles act as antennas to capture light energy and transfer it to the nearby catalytic reactor through near-field optical effects.

The research team led by Dr. Katsutoshi Nagaoka and Dr. Katsutoshi Sato has developed a fast-start ammonia hydrogen production process, which can achieve continuous supply of hydrogen without external heat. The research team found that hydrogen production at room temperature can be achieved by adding a pretreated  $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$  catalyst to the ammonia and oxygen system. The heat is transferred to the catalyst through ammonia adsorption, and the temperature is continuously increased to the catalytic reaction temperature of ammonia, and hydrogen is generated through the oxidative decomposition of ammonia. Once started, this process can proceed spontaneously to produce hydrogen. This will help to further develop the production of high-efficiency carbon-free energy and make certain contributions to solving the global energy crisis and climate issues. In the future, more coupling technologies and new high-efficiency catalysts will be produced and used in the application of ammonia decomposition to produce hydrogen.

## **3.5 Hydrogen production by cracking light hydrocarbons (propane, ethane)**

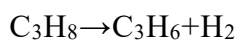
### **3.5.1 Overview**

There are two main routes for producing hydrogen by cracking light hydrocarbons, propane dehydrogenation (PDH) and ethane cracking. In fact, hydrogen is a non-target product in the production of ethylene and propylene. Ethane cracking ethylene plants are mainly concentrated in North America, the Middle East and Southeast Asia. Starting in 2017, Chinese companies have

developed the ethane-to-ethylene market, and many companies have successively announced that they will introduce low-cost light hydrocarbon feedstocks from the United States to produce ethylene. The domestic ethane cracking project is accelerating its implementation. By the end of 2022, according to the incomplete statistics, the domestic ethylene production capacity will reach  $8.58 \times 10^6$  t, and the by-product hydrogen will be  $5.534 \times 10^5$  t (1 t ethylene by-product 64.5 kg hydrogen), which can theoretically supply  $2.2 \times 10^6$  fuel cell vehicles.

### 3.5.2 Principle and process

From propane dehydrogenation to propylene reaction equation:



The traditional steam thermal cracker (ethylene plant) mainly includes C-C and C-H interrupts to produce ethylene and propylene. The temperature is  $800 \sim 920^\circ\text{C}$ , the conversion rate is  $\sim 93\%$ , the yield of ethylene is  $\sim 42\%$ , and the yield of propylene is  $\sim 17\%$ . When there is a catalyst, the reaction temperature of propane dehydrogenation is  $590 \sim 630^\circ\text{C}$ , the single-pass conversion rate is  $33\% \sim 44\%$ , and the selectivity is  $\sim 86\%$  [40]. In addition to propane and hydrogen, propane dehydrogenation has impurities  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4+$ , etc. This section mainly introduces the related technologies of propane dehydrogenation.

The thermodynamic properties of the reaction are: (1) endothermic reaction. (2) The equilibrium constant increases with the increase of temperature. Appropriate high reaction temperature. (3) Reversible reactions with increased molecular number. The lower the reaction pressure, the more favorable. Therefore, increasing the reaction temperature and reducing the pressure are conducive to the positive reaction. But too high reaction temperature will result in non-catalytic thermal cracking and deep dehydrogenation reaction intensified, resulting in lower selectivity. The temperature of catalytic dehydrogenation reaction is usually controlled at  $590 \sim 630^\circ\text{C}$ . At present, the main propane dehydrogenation technologies are Catofin process, Oleflex process and Star process. The process flow diagram is shown in Figure 1.25 [40].



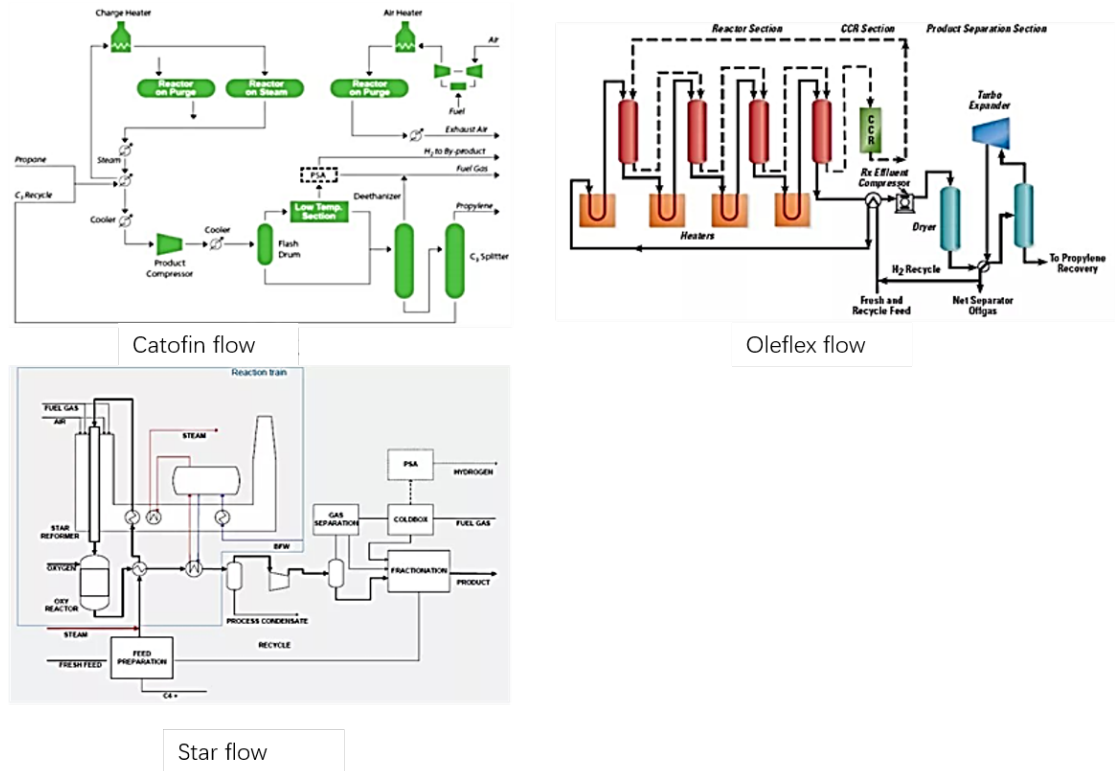


Figure 1.25 Catofin process, Oleflex process and Star process diagram

For different technological processes, the structure of the reactor involved is also quite different. The reactor structure of the three typical processes is shown in Figure 1.26.

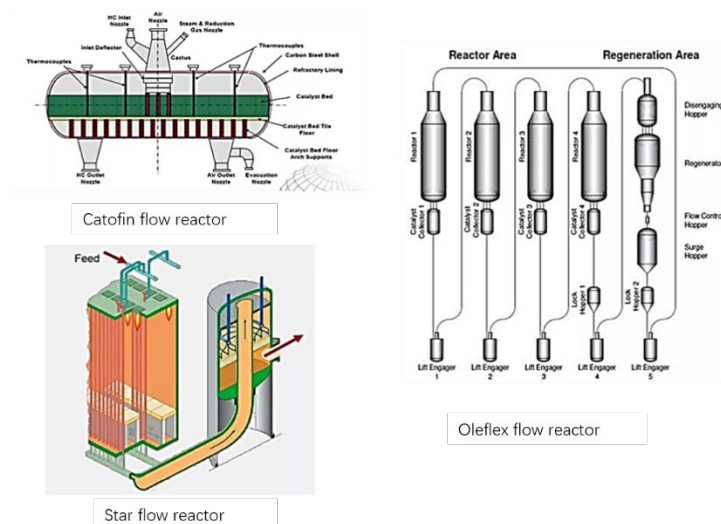


Figure 1.26 Schematic diagram of Catofin process, Oleflex process and Star process reactor

Different production processes and operating conditions used are very different. The detailed Catofin process and Oleflex process comparison are shown

in Table 1.9.

**Table 1.9 Comparison of Catofin process and Oleflex process parameters**

No.	Reactor parameters	Oleflex	Catofin
1	Shape	Moving bed	Fixed bed
2	amount/desk	4	8
3	Operation method	continuous	Loop operation
4	size	Φ3.2m~4.2m	Φ7.9m×17.2m
5	Operating temperature /℃	639-650	590-600
6	Operating pressure /MPag	0.23	-0.05
7	set tempreture /℃	670	400 (shell)
8	design pressure /MPag	0.65/F.V.	0.28/F.V.
9	Equipment material	304S.S	C.S&Refractory Lining
10	Heating (heat storage) pressure	Heating furnace heating reaction raw materials	Hot air heating catalyst + heating furnace moderately heating reaction raw materials
11	catalyst	Pt catalyst provided by UOP	Cr-based catalyst provided by Southern Chemical Company
12	Catalyst regeneration method	Continuous regeneration (CCR)	Intermittent switching regeneration

### 3.5.3 Development status

The main domestic ethane dehydrogenation and propane cracking hydrogen production enterprises under construction and already in operation are shown in tables 1.10 and 1.11. The hydrogen produced by-product of PDH device has high purity and low purification difficulty, and most of its production capacity is close to the eastern coastal area, which is closely related to the downstream fuel cell application market and has broad prospects. Up to the end of June 2019, 10 PDH projects have been put into operation in China, and 4 are under construction. There are still many PDH projects in enterprises in the preliminary work, of which 4 are planned for the exact year of production. It is expected that by the end of 2023, the total propylene production capacity of 18 PDH projects in China will reach  $1.035 \times 10^7$  t/a, and the byproduct hydrogen will be  $3.9 \times 10^5$  t/a, which can theoretically supply  $1.56 \times 10^6$  t fuel cell vehicles. In addition, propane dehydrogenation and ethane cracking units are basically concentrated in coastal port areas. Through further low investment intensity refining processes,

impurities such as total sulfur and CO in hydrogen can meet the hydrogen standard for fuel cell vehicles. Therefore, hydrogen produced by propane dehydrogenation and ethane cracking will be one of the most potential hydrogen sources for fuel cell vehicles in the future.

**Table 1.10 Domestic ethane cracking capacity**

company	project's venue	Project Progress	(Expected) Put into production time	Ethylene production capacity ( $\times 10^4$ t/Year)
Xinpu Chemical	Taixing, Jiangsu	Under construction	2019	78
Huatai Shengfu	Ningbo, Zhejiang	Under construction	2019	50
Satellite Fossil Phase I	Lianyungang, Jiangsu	Under construction	2020	125
Evergreen Holdings	Futian Putian	Proposed	2020	150
Luqing Petrochemical	Shouguang, Shandong	Proposed	2021	75
Nanshan Group	Longkou, Shandong	Proposed	2021	100
PetroChina Bazhou	Bazhou, Xinjiang	Proposed	2021	60
Guangxi Investment Group	Qinzhou, Guangxi	Proposed	2021	60
Wanhua Chemical	Yantai, Shandong	Proposed	2022	60
Dalian Huikun New Materials	Dalian, Liaoning	Proposed	2022	100
total				858

**Table 1.11 Domestic production capacity of propane cracking**

company	project's venue	Project Progress	(Expected) Put into production time	Propylene production capacity ( $\times 10^4$ t/Year)
Tianjin Bohua	Tianjin	Put into production	2013	60
Satellite Petrochemical Phase I	Ningbo, Zhejiang	Put into production	2014	45
Ningbo Haiyue New Material Phase I	Ningbo, Zhejiang	Put into production	2014	60
Shaoxing Sanyuan Petrochemical	Shaoxing, Zhejiang	Put into production	2014	45
Donghua Energy Zhangjiagang Yangtze River Petrochemical	Zhangjiagang, Jiangsu	Put into production	2015	60
Wanhua Nickel	Yantai, Shandong	Put into production	2015	75
Donghua Energy Ningbo New Materials Phase I	Ningbo, Zhejiang	Put into production	2016	66
Hebei Haiwei	Hengshui, Hebei	Put into production	2016	50
Fujian Meide Petrochemical	Fuzhou, Fujian	Put into production	2018	66
Satellite Petrochemical Phase II	Pinghu, Zhejiang	Put into production	2019	45
Donghua Energy Ningbo New Materials Phase II	Ningbo, Zhejiang	Under construction	2019	60
Shenzhen Juzheng Energy	Guangdong Dongguan	Under construction	2020	66
Hebei Haiwei Lanhang Chemical Industry	Cangzhou, Hebei	Under construction	2020	50
Jiangsu Weiming Petrochemical	Rudong, Jiangsu	Under construction	2021	60
Henan Nanpu Environmental Protection	LuoYang HeNan	Under construction	2021	46.62
Xuzhou Haiding Chemical	Pizhou, Jiangsu	Under construction	2022	60
Jinneng Technology	Qingdao, Shandong	Under construction	2023	90
Binhua New Materials Phase I	Binzhou, Shandong	Under construction		60
total				1035

In the catalytic dehydrogenation process, the catalysts used are generally supported noble metal platinum or toxic chromium-based catalysts. The platinum-based catalysts are expensive and the raw materials need to be deeply purified, while the chromium-based catalysts are harmful to the environment and human body. Therefore, the development of low-cost, environmentally friendly non-

noble metal catalysts has been a technical problem for propane dehydrogenation. At present, platinum-based catalysts are the key to catalytic dehydrogenation, and related technologies have been monopolized by the United States, Germany and other countries for a long time. The existing 12 sets of propylene production lines for propane dehydrogenation in China are imported from abroad at high prices, and the catalysts are also completely dependent on imports. However, this situation is expected to be broken. Tianjin University Energy Chemical Engineering Team has successfully developed efficient platinum-based catalysts, which can significantly improve the production efficiency of propylene. Whoever has more efficient catalysts will master the future of olefin industry. Platinum-based catalysts have been widely used in the production of propylene by propane dehydrogenation, and the principle is to use platinum and other metals to extract and produce propylene by catalytic dehydrogenation selectivity. The high-efficiency platinum-based catalyst developed by the energy and chemical engineering team of Tianjin University has two new advantages. First, it is “more pure”, the metal impurities of the promoter are removed by high temperature reduction and pickling, so that the catalyst forms the core-shell surface covered by pure platinum. Second is “stronger”, by changing the electronic state of platinum on the surface, the catalytic activity of platinum atom is greatly improved, which creates a possibility for greatly improving the production efficiency of propylene in industrial practice and opens up a new idea for the application of platinum-base catalysts.

## 4. Biomass hydrogen production

Biomass hydrogen production is a method of hydrogen production that uses biomass from photosynthesis as raw materials by chemical or biological methods. It can use surplus waste organic matter in pulping and papermaking, biorefinery, and agricultural production as raw materials, because its advantages of energy saving and cleanness, it has become a research hotspot in the field of hydrogen production <sup>[43]</sup>. At present, hydrogen production methods using biomass as the raw materials include chemical hydrogen production and biological hydrogen production (Figure 1.27). The most common hydrogen production methods include gasification and microbial hydrogen production. This section mainly introduces these two biomass production methods. Hydrogen method related content, and briefly introduce other biomass hydrogen production methods.

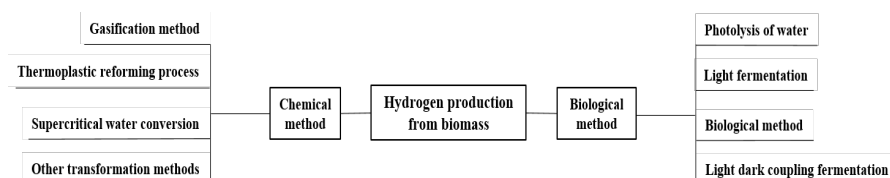


Figure 1.27 Biomass hydrogen production method

### 4.1 Biomass gasification hydrogen production

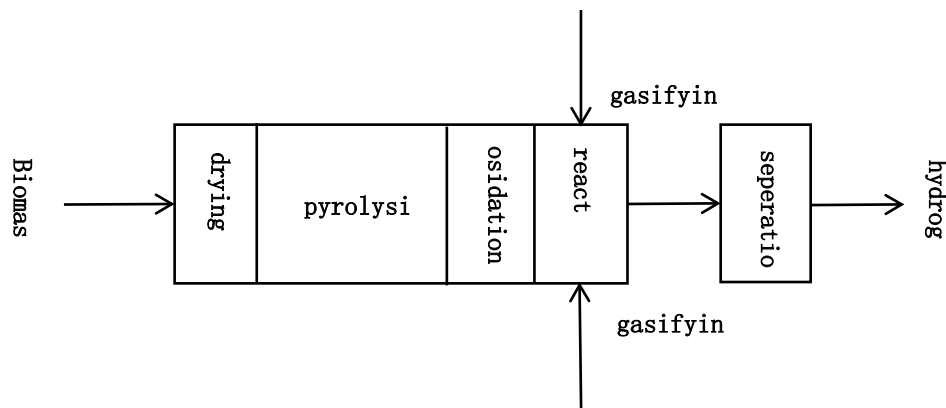
#### 4.1.1 Overview

Pressing biomass raw materials such as firewood, sawn grass, wheat straw, rice straw, etc. into a gasification furnace (or cracking furnace) can be gasified or cracked to produce hydrogen-containing fuel gas, that is, biomass gasification for hydrogen production. The research in the field of biomass gasification technology has achieved certain results in China. Guangzhou Institute of Energy, Chinese Academy of Sciences has conducted several researches on biomass gasification over the years. The gasification product contains about 10% of hydrogen and has a calorific value of  $11\text{MJ}\cdot\text{m}^{-3}$ . This result proves that although fuel gas can be used as a living fuel in rural areas, its hydrogen content is relatively low. In foreign countries, due to the improvement of conversion technology, biomass gasification has been able to produce water gas on a large scale, and its hydrogen content has greatly increased <sup>[44]</sup>.

### 4.1.2 Principle and process

Hydrogen production by gasification refers to the process of converting hydrocarbons into combustible gases containing hydrogen in gasification agents (such as air, water vapor, etc.), but this technology also has the problem of uncontrollable tar. At present, the hydrogen production from biomass gasification requires the help of catalysts to accelerate the medium and low temperature reactions. The reactors used in biomass gasification to produce hydrogen are divided into: fixed bed, fluidized bed, and entrained bed gasifier.

The process of hydrogen production by gasification is shown in Figure 1.28. Biomass enters the gasification furnace to be heated and dried, and evaporates water (100-200°C). As the temperature rises, the material begins to decompose and produce hydrocarbon gas. Subsequently, the coke and pyrolysis products undergo an oxidation reaction with the gasification agent passed in. As the temperature further increases (800-1000°C), the oxygen in the system is exhausted and the products begin to be reduced, mainly including the Boudouard reaction, water gas reaction, methanation reaction, etc<sup>[45]</sup>.



**Figure 1.28 Flow chart of biomass gasification hydrogen production**

Biomass gasification agents mainly include air, water vapor, and oxygen. When oxygen is used as the gasification agent, the amount of hydrogen produced is high, but the preparation of pure oxygen consumes a lot of energy. Although the cost is low when air is used as the gasification agent, there is a large amount of nitrogen that is difficult to separate. Table 1.12 shows the effects of different gasification agents on the performance of biomass hydrogen production <sup>[46]</sup>.

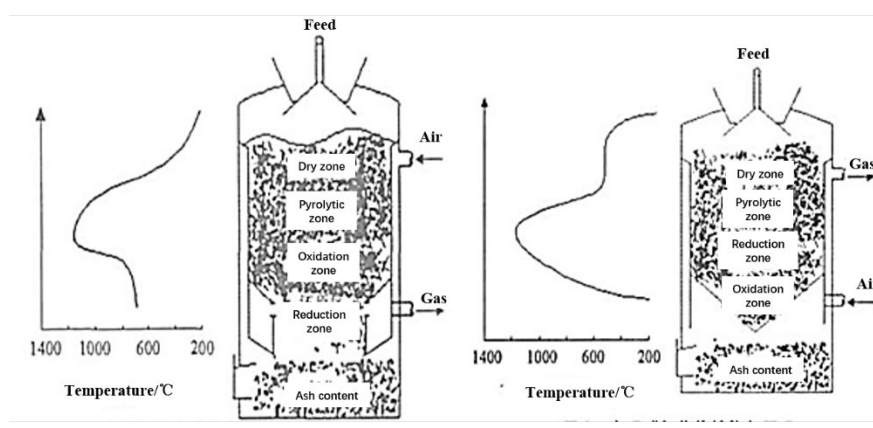
**Table 1.12 Hydrogen production under different gasification agents**

Gasification agent	Hydrogen production		Hydrogen content	Cost class
	Calorific value of gas production (MJ·M <sup>-3</sup> )	Total gas yield (KG·M <sup>-3</sup> )		
water vapor	12.2-13.8	1.30-1.60	38.0-56.0	medium
Air and water vapor mixture	10.3-13.5	0.86-1.14	13.8-31.7	high
air	3.7-8.4	1.25-2.45	5.0-16.3	low

Biomass gasification is divided into fixed bed gasification and fluidized bed gasification according to the flow velocity and direction of combustible gas relative to material in the gasifier. In the fixed bed gasifier, the gasification reaction of materials is carried out in a relatively static bed, which is compact in structure, easy to operate and has high thermal efficiency.

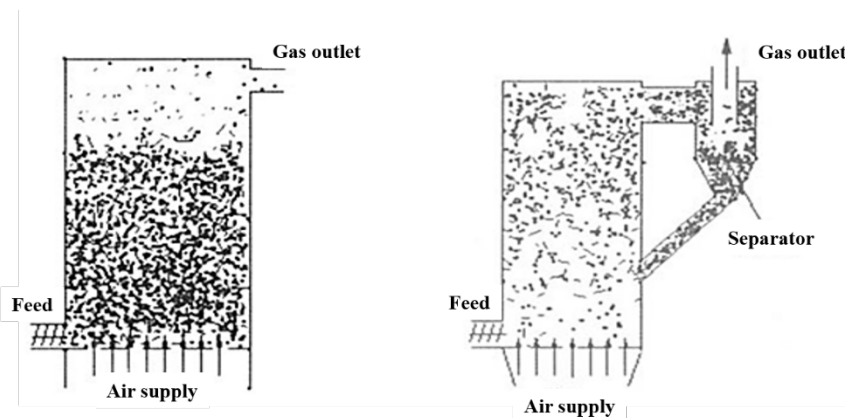
The fixed bed gasifier has a furnace chamber containing raw materials and a grate supporting the reaction layer. The down suction gasifier and up suction gasifier are widely used. As shown in Fig. 1.29, in the downdraft gasifier, the raw material was added from the upper part and dropped by gravity. After passing through the drying zone, the water was evaporated and entered the thermal decomposition zone with high temperature to generate carbon, cracked gas, tar and so on. Then, the coke and tar were transformed into CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> through the redox zone. The operating temperature in the furnace was about 400–1200°C. The is absorbed from the lower part of the reaction layer and the ash is discharged from the bottom. The downdraft gasifier works stably, and part of the tar generated by gasification can be decomposed into permanent small molecule gases when passing through the lower high temperature zone, which increases the calorific value of the gas and reduces the tar content in the outgoing gas. In the up-suction gasifier, the moving direction of raw material is opposite to that of airflow. The gasification agent enters the gasifier from the bottom inlet of the furnace body to participate in gasification. The generated gas flows from bottom to top and is discharged from the gas outlet. The ash content of the gas from the furnace is less, and the gasification efficiency is higher. However, there are also problems such as difficult sealing and inconvenient feeding <sup>[47]</sup>.





**Figure 1.29 Schematic diagram of the structure and principle of the upper and lower gasifier**

Under the action of the blowing gasification agent in the fluidized bed gasifier, the material particles, sand, gasification medium and other objects have fully contact with each other, and the heating is uniform. The fluidized bed gasifier is boiling in the furnace, and the gasification reaction is fast with high gas production rate. Compared with the fixed bed, the fluidized bed has no grate. A simple fluidized bed is composed of a combustion chamber and an air distributor, and the gasification agent enters the fluidized bed reactor through the air distributor. According to the structure and gasification process of the gasifier, the fluidized bed can be divided into bubbling fluidized bed and circulating fluidized bed, as shown in Fig. 1.30 [47].



**Figure 1.30 Schematic diagram of the principle of bubbling bed and circulating bed**

### 4.1.3 Development status

At present, the catalysts for tar cracking of biomass gasification that have

been studied at home and abroad include dolomite, nickel-based catalysts and alkali metal catalysts. When dolomite is used in biomass gasification, it is widely used because of its high efficiency in removing tar, low cost and high practical value. It can be directly mixed with biomass before gasification, or it can be placed in a downstream reactor as a guard bed. Scholars at home and abroad have conducted in-depth research on this, and the research results prove that it is the most studied biomass gasification field. catalyst. Nickel-based catalysts can reform hydrocarbons and adjust the composition of gas products in the cracking of biomass tar, and have a high cracking rate at 750°C, which has a good catalytic effect. However, the carbon deposition and sintering on the catalyst surface will cause the nickel-based catalyst to lose its activity, but its performance can be improved by adding a co-catalyst. Many researchers have done a lot of work for this. Aznar and other studies have shown that commercial nickel-based catalysts can make the conversion rate of biomass tar reach more than 99%, and can adjust the composition of gas products. Alkali metal catalysts are generally mixed with biomass raw materials into the gasification furnace, and its recovery is difficult, and it will increase the amount of ash discharged from the gasification furnace, which affects the further development of alkali metal catalyst technology. Encinar et al. studied the catalytic cracking of alkali metal chlorides in tar, and analyzed the effects of various catalysts and their concentrations on gasification. Mudge et al. studied the effects of several alkali metal carbonates and natural minerals on the activity of catalyzing water vapor gasification of wood chips <sup>[47]</sup>.

Zhang et al. used potassium salt as a catalyst to increase the conversion rate of carbon in biomass, and discussed the effects of reaction temperature and catalyst type on hydrogen production by gasification. Studies have shown that both  $K_2CO_3$  and  $CH_3COOK$  can promote hydrogen production by gasification at 600-700°C. At 700°C, when the  $K_2CO_3$  dosage is 20%, the carbon conversion rate reaches 88%, and the hydrogen content in the gas obtained at this time is 73%. With KCl as the catalyst, the carbon conversion rate and hydrogen yield in the biomass gasification process show a downward trend, and it is concluded that the use of KCl should be avoided in the biomass gasification <sup>[48]</sup>.

Using oxygen as the gasification agent, Hamad et al. discussed the effects of oxygen consumption, gasification residence time, and catalyst type on hydrogen

production. The results show that when the mass ratio of oxygen to raw material is 0.25, the gasification stays for 90 min, and the roasted cement kiln dust or slaked lime is used as the catalyst, the biomass can achieve a good gasification effect. When cotton stalk was used as the research object and slaked lime was used as the catalyst, the content of hydrogen and carbon monoxide in the gasification products reached 45% and 33%, respectively [49].

Sun Ning et al. used pine sawdust as raw material, steam as gasification agent, and used nickel-based composite catalyst Ni-CaO to perform gasification reaction in a fixed-bed gasifier. When the catalyst raw material mass ratio increases from 0 to 1.5, the hydrogen volume fraction increases from 45.58% to 60.23%, and the hydrogen yield increases from  $38.80 \text{ g} \cdot \text{kg}^{-1}$  raw material to  $93.75 \text{ g} \cdot \text{kg}^{-1}$  raw material; when the temperature is raised from  $700^{\circ}\text{C}$  to  $750^{\circ}\text{C}$ , the volume fraction of hydrogen in the fuel gas increases from 54.24% to 60.23%, the carbon dioxide content decreases from 21.09% to 13.18%, and the gas heat value is  $12.13 \text{ MJ} \cdot \text{m}^{-3}$  [50, 51].

China attaches great importance to the utilization of biomass energy, and has listed the research and application of biomass energy utilization technology as a key project in four national five-year plans, and has made positive progress in the research and development of biomass gasification and gasification power generation. Jintongling and Jixian Government of Shuangyashan City, Heilongjiang Province signed the *“Cooperation agreement of biomass gasification hydrogen extraction and cogeneration project in Jixian County, Shuangyashan City, Heilongjiang Province”* in Nantong. The project of biomass gasification and hydrogen extraction and cogeneration with the total annual hydrogen production of  $2 \times 10^8 \text{ m}^3$  in Jintongling has been approved by the Development and Reform Commission. The project was started in September 2019, and the project planned to invest CNY  $1.32 \times 10^9$  yuan [52]. A large number of outstanding scientific research achievements and application technology into the market, small and medium-sized centralized gas supply, heating and gasification power generation has entered the practical stage, so that China's biomass conversion technology has been rapid development. In the future, the main factors hindering the commercial operation of biomass gasification technology will be systematically analyzed, the key technologies and related

supporting technologies and facilities of biomass gasification will be solved as soon as possible, and the pilot demonstration project of new technologies with scale benefits will be actively established to solve the convergence problem between technology, market and policy, clarify the laws, tax policies and financial support methods, and vigorously promote the development of biomass gasification technology in China.

## **4.2 Microbial hydrogen production**

### **4.2.1 Overview**

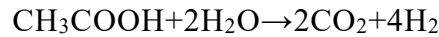
Microbial hydrogen production technology has also attracted people's attention. Hydrogen can be produced by enzymatic reaction under normal temperature and pressure. There are mainly two ways of hydrogen production from biomass, which are chemical energy nutrition microorganism and photosynthetic microorganism. Some strict anaerobic bacteria and facultative anaerobic bacteria of various fermentation types belong to chemotrophic microorganisms, and the original substrate for hydrogen release of fermentation microorganisms is various carbohydrates and proteins. At present, there are patents for hydrogen production using carbohydrate fermentation, and the generated hydrogen is used as the energy for power generation. The hydrogen production process of photosynthetic microorganisms such as microalgae and photosynthetic bacteria is associated with photosynthesis, which is called photosynthetic hydrogen production. In the early 1990s, the Institute of Microbiology of the Chinese Academy of Sciences, Zhejiang Agricultural University and other units conducted "Isolation and Screening of Hydrogen-producing Purple Non-sulfur Photosynthetic Bacteria" and "Study on Hydrogen Production in the Process of Immobilized Photosynthetic Bacteria Treating Wastewater" and achieved certain results. An optimized bioreactor using photosynthetic bacteria to produce hydrogen has also been designed abroad, and its scale will reach a daily hydrogen production of  $2.8 \times 10^3 \text{m}^3$ . The method uses various industrial and domestic organic wastewater and waste materials of agricultural and sideline products as a substrate to carry out continuous cultivation of photosynthetic bacteria, and can purify wastewater and obtain single-cell protein while producing hydrogen. It achieves three goals with one

stone and has a bright future.

#### 4.2.2 Principle and process

Microbial hydrogen production involves a variety of models, involving a variety of biomass substrates. This section mainly introduces methods for hydrogen production by light fermentation, hydrogen production by dark fermentation, hydrogen production by sludge, hydrogen production by food waste, and microbial fuel cells.

(1) Photofermentation is a biological process of photosynthetic bacteria. Photosynthetic non-sulfur bacteria (PNS) use organic acids or volatile fatty acids (VFA) as substrates and use carbon dioxide as a by-product to produce hydrogen. Carbon sources, such as glucose, can also be used for hydrogen production by PNS bacteria. The main photosynthetic organisms include Oscillating Bacteria and *Rhodospirillum rubrum*. The photo-fermentation reaction process is:



The core mechanism of photosynthetic microorganisms producing hydrogen is shown in Figure 1.31: In a strict anaerobic environment, the colony needs to have enough surface area to absorb enough sunlight to ensure the normal progress of the photo-fermentation process. In addition, controlling the operating conditions for efficient hydrogen production by photo-fermentation cannot be ignored. In addition to sufficient sunlight and anaerobic environment, pH value, temperature and the content of certain metal elements required by nitrogenase to form  $\text{H}_2$  are also important factors to be considered [53].

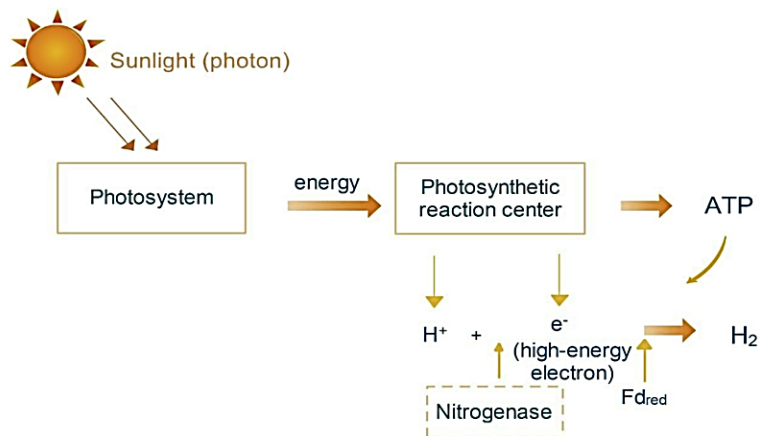


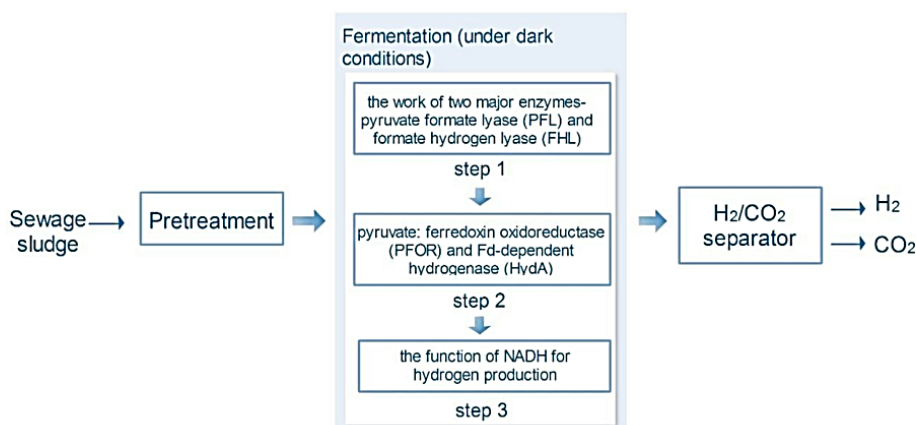
Figure 1.31 The core mechanism of photosynthetic microorganisms

### producing hydrogen

(2) Dark fermentation means that bacteria degrade carbohydrates (mainly glucose) under the action of nitrogenase or hydrogenase under dark and hypoxic conditions, and react with VFAS and CO<sub>2</sub> to generate hydrogen. Organic substances, such as formic acid, pyruvate, and other short-chain fatty acids, are also common substrates for dark fermentation. Some widely used cultures such as spore-forming *Clostridium* (eg. *Clostridium butyricum*), *Bacillus* and various thermophilic microorganisms. Choosing glucose as the substrate, the related reaction can be expressed as [54]:

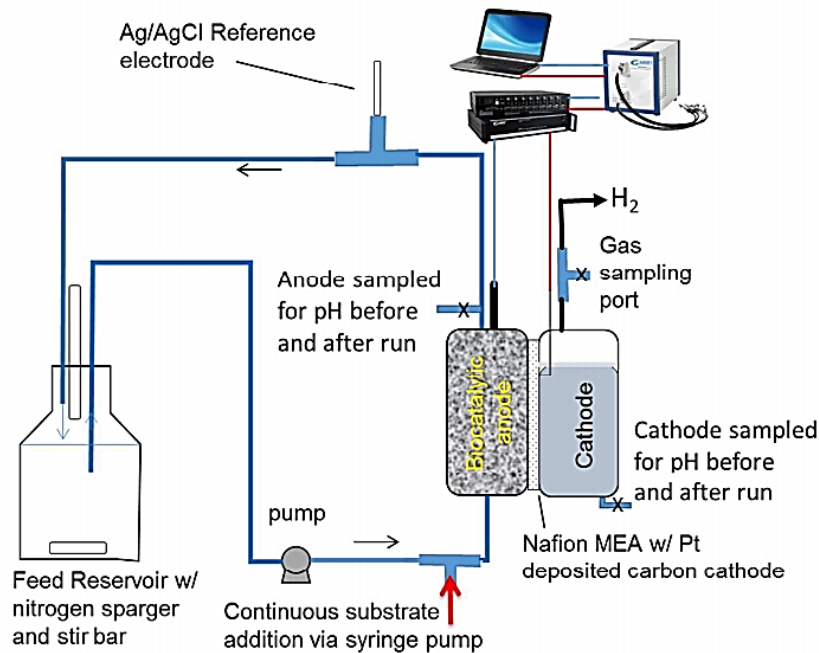


The main steps of dark fermentation are shown in Figure 1.32:



**Figure 1.32 Flow chart of hydrogen production from sludge dark fermentation**

The main research results and development directions of existing anaerobic fermentation hydrogen production include: (1) Hydrogen production by anaerobic fermentation of sludge; (2) Hydrogen production by high-efficiency hydrogen-producing bacteria. In the process of anaerobic fermentation, hydrogen-producing bacteria and other microorganisms use sugar as carbon and energy sources, and use protein and amino acids in wastewater as nitrogen sources and vitamins, plus other rich nutrients in the wastewater. Good growth and reproduction, thereby producing hydrogen. The typical process is shown in Figure 1.33.。



**Figure 1.33 Hydrogen production process from microbial fermentation products**

(3) Hydrogen production by anaerobic fermentation of sludge. Cultivating hydrogen-producing sludge is the basis and key to the experimental research on hydrogen production by anaerobic fermentation. Sludge is a mixture of various microorganisms, including both hydrogen-producing microorganisms and hydrogenophilic microorganisms. In the anaerobic fermentation process, the hydrogen produced by the hydrogen-producing microorganisms will be quickly used by the hydrogenophilic microorganisms. However, some hydrogen-producing microorganisms can form spores, and their ability to withstand adverse environmental conditions is stronger than ordinary microorganisms. Taking advantage of the difference in the living conditions of these two types of microorganisms, pretreatment (such as heat treatment, acid treatment and alkali treatment, etc.) can inhibit the hydrogen-consuming microorganisms in the sludge, so as to achieve the purpose of screening hydrogen-producing microorganisms [55].

In the past, most studies on hydrogen production by anaerobic fermentation focused on pure strain screening and cell immobilization technology. The separation and purification technology of strains is harsh and difficult to obtain in batches, and the cost is high, which is only suitable for laboratory research. Small-scale experiments are easy to obtain instantaneous high hydrogen yield,

but long-term operation and continuous hydrogen production, maintain high yield and concentration, it will be difficult to make breakthroughs because of high technical difficulties. In addition, the immobilization technology is complex and it is difficult to select the appropriate embedding agent. After cell immobilization, the mass transfer resistance inside the particles is large, and the metabolites accumulated in the particles will inhibit the cells, thereby reducing the hydrogen production capacity. Therefore, the application and large-scale production of hydrogen production by pure strain and cell immobilization technology are restricted [56].

Organic matter in sewage treatment plant is mainly carbohydrates, proteins, amino acids, fatty acids, oils, esters and other substances. Therefore, in principle, it is completely feasible to convert the organic matter in the sewage of the sewage treatment plant into hydrogen by microbial fermentation. However, there is a problem. At present, most hydrogen-producing strains are glucose-based carbohydrates as the substrate, and all organic matters cannot be converted, so the ability to reduce the amount of sewage treatment in sewage treatment plants is weak. Moreover, through microbial fermentation, the hydrogen production rate is slow and the production cycle is long. In addition, the requirements of microbial survival for the environment (temperature, pH, etc.) are relatively high, and the corresponding maintenance costs are large.

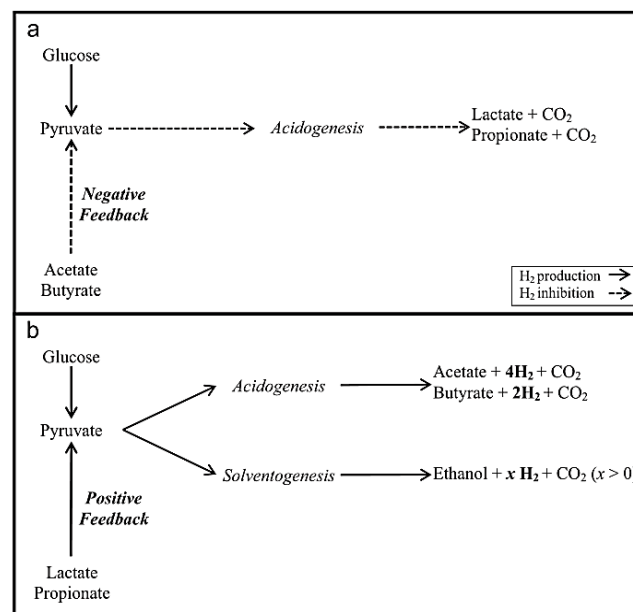
**Table 1.13 Typical types of hydrogen production and hydrogen production capacity [57]**

Biological group	Hydrogen production efficiency [mol H <sub>2</sub> mol substrate]	Biological group	Hydrogen production efficiency [mol H <sub>2</sub> mol substrate]
Strictly anaerobic bacteria	2(glucose)	Thermophilic archaea	4(Acetic acid)
Facultative anaerobic bacteria	0.35(glucose)	Photosynthetic bacteria	7(Succinic acid)
Azotobacter	1.05~2.2(glucose)	Photosynthetic bacteria	7(Malic acid)
Rumen bacteria	2.37(glucose)	Cellulolytic bacteria	6.2(Cellulose)
Aerobic bacteria	0.7(glucose)	Cyanobacteria	20mL·(g·h) <sup>-1</sup>

Organic acids are the promoters or inhibitors of H<sub>2</sub> production. Acetic acid and butyric acid production are usually associated with high H<sub>2</sub> production, but their accumulation will have a negative impact on H<sub>2</sub> production. For example, it



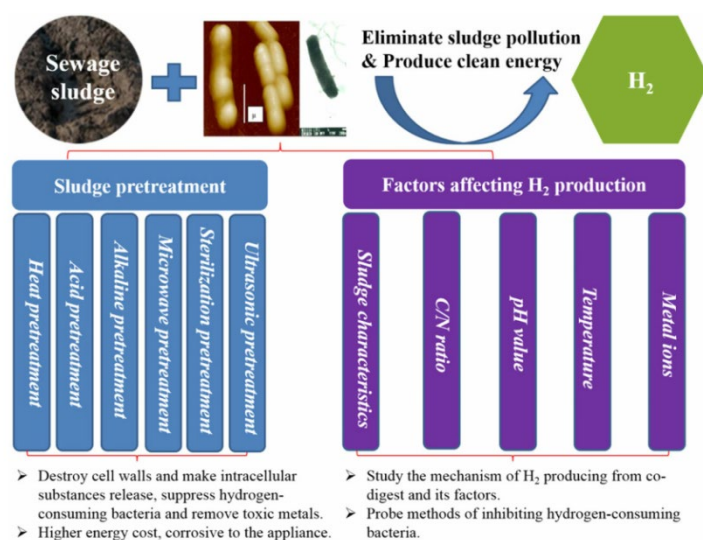
has been found that excessive addition of butyric acid inhibits the production of  $H_2$  from kitchen waste, while excessive acetic acid inhibits the production of  $H_2$  from glycerol. On the contrary, such as lactic acid and propionic acid, when they exist at the threshold concentration, they can be used as potential promoters. When added to the fermentation broth, lactic acid and propionic acid can trigger benign reactions (Figure 1.34), and induce more  $H_2$  production through pyruvic acid pathway. It is reported that the addition of lactic acid at  $650 \text{ mg} \cdot \text{L}^{-1}$  can increase the hydrogen production up to 37%, while the propionate can increase the hydrogen production by 28% [58].



**Figure 1.34 The relationship between fermentation products and hydrogen production (a) Accumulation of acetic acid/butyric acid inhibits  $H_2$  (b) Promotion of lactic acid and propionic acid**

The advantages and challenges of hydrogen production from sludge, co-digestion of sludge is promising, and more substrates can be applied, such as kitchen waste, plant straw, livestock and poultry manure, etc. However, the mechanism, influencing factors and technical and economic evaluation of hydrogen production by digestion need to be further studied (Figure 1.35). This technology is still in its infancy and is mainly applied on an experimental scale. Due to the problems of low hydrogen production rate and high cost, it is difficult to realize industrialized mass production. The hydrogen production rate is about 20% to 30% of the theoretical output, which is significantly lower than the economically feasible level of 60% to 80%. Therefore, to translate this research

into a commercial reality, further research is needed. For example, a certain degree of hydrogen consumption occurs in the final stage of the hydrogen production process. How to inhibit hydrogen-consuming bacteria without affecting the activity of hydrogen-producing bacteria is a problem worthy of study. At present, most researches on hydrogen production are batch experiments, and the amount of hydrogen production is not large [59].



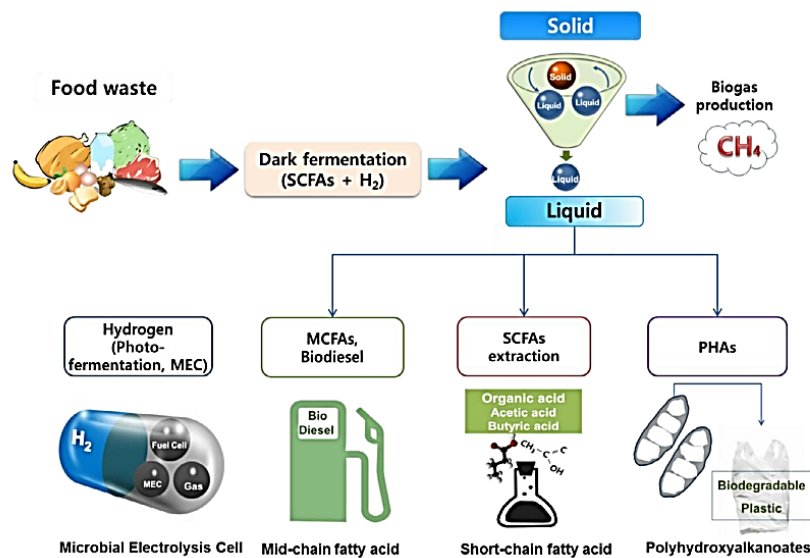
**Figure 1.35 Advantages and challenges of hydrogen production from sludge**

(4) Hydrogen production from food waste. Among various biological hydrogen production pathways, dark fermentation is considered to be the most practical way because of its strong ability to degrade organic waste and high hydrogen production rate. Food Waste (FW) has a high carbohydrate content and is easily hydrolyzed, and has a higher hydrogen production potential than other organic waste [60].

However, reports on pilot and large-scale research on FW dark fermentation are quite limited. The scale of the fermentation tank is  $0.15\sim0.5\text{ m}^3$ , which is far smaller than the actual scale. Full mixing in a laboratory-scale fermentor can ensure uniformity, thereby achieving precise pH control. However, when scale-up and actual implementation, it is uncertain whether the pH value of the entire fermenter is uniform. In the case of insufficient stirring, there may be a dead zone, which may reduce the accuracy of pH control, resulting in a reduction in  $\text{H}_2$  production. In order to design the agitator and mix effectively, it is important to fully understand the rheological properties such as viscosity, storage and loss

modulus. These values are not constant, and they vary with solids concentration, temperature, shear rate, and raw material type.

Although the  $H_2$  yield of FW is limited, Dark Fermentation Effluent (DFE) can be further used for valuable fuel and chemical processing. After FW dark fermentation is successful, it contains short-chain fatty acids such as acetic acid and butyric acid (SCFA, Figure 1.36), which account for 40-60% of FW energy. These single-chain fatty acids can be further processed into  $H_2$  by MEC and light fermentation. People have conducted extensive research on the process of combining “dark fermentation and light fermentation” to obtain high  $H_2$  yield, but the research on using FW as a raw material is still limited.



**Figure 1.36 Integrated system of kitchen waste dark fermentation and sewage conversion process (SCFAs: short-chain fatty acids, MEC: microbial electrolytic cells, MCFAs: medium-chain fatty acids, PHAs: polyhydroxyalkanoic acid)**

(5) Microbial fuel cell. Microbial fuel cell is a new device that uses microorganisms as a catalyst to decompose biomass through oxidation and simultaneously output electrical energy (Figure 1.37). At the beginning of the 20th century, botanists discovered that experiments with yeast and *E. coli* can generate electric current <sup>[61]</sup>. In 1984, American scientists used urine and living biological bacteria to invent a bacterial battery that can be applied to spacecraft, but the effective utilization rate of this battery is very low. At the same time, British chemists conducted experiments on the decomposition of bacteria in the

battery pack. The electrons released during the experiment reached the anode through movement to generate electricity.

As mentioned above, biological hydrogen production is a promising method of hydrogen production, which can be achieved through bioelectrochemical systems (BESs). BESs have a wide range of applications in wastewater treatment, gas production ( $H_2$ ,  $CH_4$ ), nutrient recovery, chemical synthesis, desalination and bioremediation. The key point of biological hydrogen production is that it produces hydrogen through oxidation-reduction reactions on the surface of microorganisms. BESs that have been extensively studied include microbial fuel cells (MFC), whose main purpose is to produce electricity, and microbial electrolytic cells (MEC), whose main purpose is to produce hydrogen. In the process of converting biological waste into  $H_2$ , MEC is first oxidized into organic matter by the electricity-generating bacteria, and then transfers the electrons to a fixed electrode. The electrons are combined with protons on the cathode through an external circuit to produce hydrogen. Generally speaking, the power of the cathode itself is slow, and it is not enough for the hydrogen evolution reaction to occur on it. Therefore, in the MEC, an external voltage (0.2V to 1.0V) is applied to promote the hydrogen evolution reaction of the cathode to produce hydrogen. Because the traditional water hydrogen production voltage is 1.2 V or more, MEC biological hydrogen production is relatively an energy-saving option.

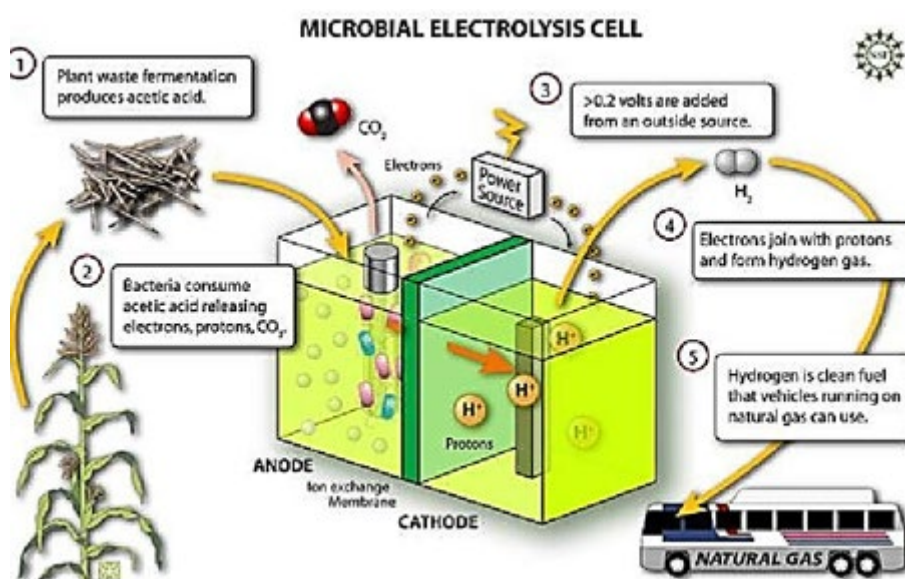
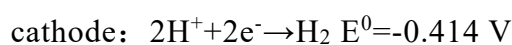
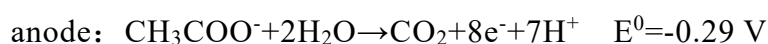


Figure 1.37 Schematic diagram of hydrogen production from biofuel cells

The specific principle of the microbial fuel cell is that in the anode chamber,

microorganisms (catalysts) decompose certain components (acetate, glucose, hydrogen, etc.) in the indoor matrix through catalytic oxidation to generate carbon dioxide, H protons, and electrons; The electrons generated in the process can be transferred to the anode surface through nanowires and intracellular transfer, and then conducted to the cathode surface through an external circuit. The H protons move through diffusion to reach the cathode chamber, and finally chemical catalysis or biocatalysis occurs in the cathode chamber. Reaction, combined with surface electrons to generate hydrogen [62].

Take acetic acid as an example:



From the thermodynamic point of view, the standard electrode potentials for anodic oxidation of acetic acid and cathodic hydrogen production are -0.290 V and -0.414 V, respectively. Therefore, in theory, only 0.124 V voltage is needed to produce the above reaction, which is far less than the theoretical voltage of 1.23 V required for traditional electrolysis of water. In practical operation, the electrode overpotential and internal resistance need to be overcome, so the actual applied voltage should be higher than 0.124 V. At present, the reported minimum voltage for hydrogen production is 0.22V, while the applied voltage of conventional electrolysis water is 1.6V [63]. Therefore, MEC is more economically feasible in hydrogen production.

There are two main types of microbial fuel cell reactors: single-chamber and double-chamber (Figures 1.38&1.39). Double-chamber reactor: in 2005, a double-chamber biological hydrogen production reactor was first proposed. The reactor uses a proton exchange membrane to separate the cathode and anode compartments. Liu et al. [64] found that about 90% of the anode chamber substrate will be consumed intermittently, and its coulombic efficiency is 78%, and the total hydrogen production efficiency is only 60-73%. There are some unavoidable side reactions and losses, such as biomass production, conversion of substrates to polymers, and hydrogen to methane and acetic acid. It is reported that the use of alkaline electrolyte in the MEC cathode can increase the hydrogen evolution rate ( $1.6 \text{ m}^3 \cdot \text{d}^{-1}$ ), because the higher the conductivity of the solution, the lower the resistance [65]. In addition, the distance between the cathode and anode also has a

great impact on this, because the short distance can reduce its internal resistance. The use of the isolation membrane can effectively reduce the diffusion of hydrogen into the anode chamber, but it also increases the complexity and cost. Therefore, in order to improve the efficiency of hydrogen production, it is particularly important to prevent hydrogen from entering the anode chamber.



**Figure 1.38 Two-chamber microbial electrolytic cell**

Single chamber reactor: hydrogen is precipitated from the cathode by reduction reaction in MEC, and the cathode conversion efficiency refers to the efficiency of electrons being converted from anode to cathode [66]. It is reported that the diffusion of hydrogen in dual chamber MEC can reduce the cathode conversion efficiency by 33%, which may be due to the diffusion of hydrogen to the anode surface or the oxidation by microorganisms. In 2007, Rozendal et al. used a single-chamber microbial electrolysis cell to produce hydrogen, and the next few years have been studied. Single chamber MEC equipment is characterized by anode and cathode in an indoor, there is no pH gradient between anode and cathode, so it has low ohmic resistance and overpotential. Call and Logan found that under the same operating conditions, the hydrogen evolution rate of single-chamber reactor was twice that of double-chamber reactor ( $3.12 \text{ m}^3 \cdot \text{d}^{-1}$ , applied voltage 0.8 V). In addition, anode and cathode in an indoor, greatly reducing the cost of equipment.



**Figure 1.39 Single-chamber microbial electrolytic cell**

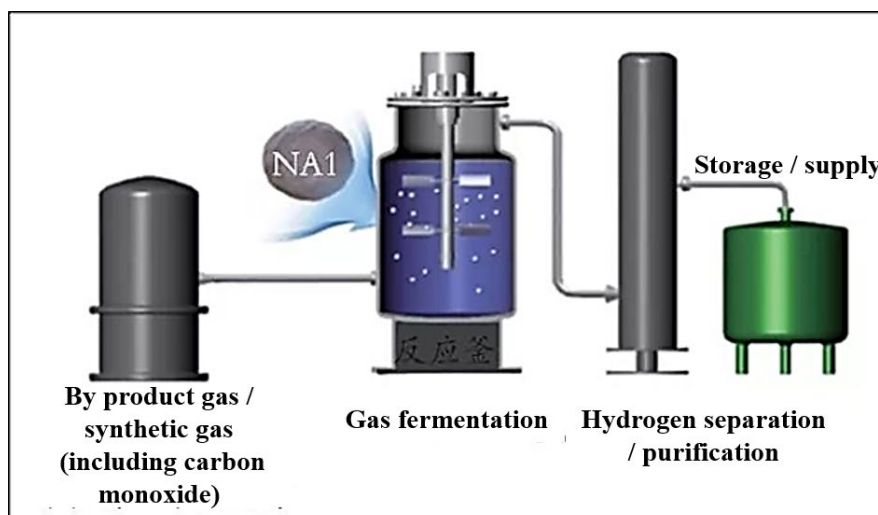
Compared with traditional thermochemistry and electrochemical hydrogen production technology, biological hydrogen production technology has the advantages of low energy consumption and less pollution. Microbial fuel cell (MFC) has lower power and hydrogen production performance than other batteries, and wastewater treatment is another breakthrough point, because the hydrogen yield can reach  $1 \text{ m}^3 \cdot \text{d}^{-1}$ , so it is suitable for hydrogen production from sewage. This makes MEC become a topic worthy of further research and development, but how to improve the hydrogen production rate in MEC is also the biggest challenge in the research process. To some extent, because waste water pollutes materials and degrades their performance, there is also part of the higher cost of waste water treatment. Therefore, cheap and readily available materials which can be used in wastewater treatment for a long time have become a research hotspot in recent years.

### **4.2.3 Development status**

Since 2009, the South Korean Ministry of Marine Fisheries and the South Korean Academy of Marine Science and Technology have jointly used marine microorganisms to develop environmentally friendly biological hydrogen production technologies. The raw materials used are mainly the tail gas generated during steel production and power generation, which is used by microorganisms to produce hydrogen. In 2010, the research team of the South Korean Academy



of Marine Science and Technology selected the ultra-high-temperature marine microorganism “NA1” (*Thermococcus onnurineus*, deep-sea hyperthermophilic archaea) as the catalyst to react with carbon monoxide, formic acid and seawater, thus successfully preparing hydrogen (Figure 1.40). In 2011–2014, a small equipment was constructed to successfully produce hydrogen using the by-product gas of the iron and steel plant. At the same time, the “NA1” was improved by breeding. The production efficiency of hydrogen increased from  $0.2 \text{ kg} \cdot \text{kL}^{-1}$  per day to  $12 \text{ kg} \cdot \text{kL}^{-1}$ , and the production efficiency increased by nearly 60 times. A 1 t pilot plant was built in 2015-2017 to produce hydrogen continuously for more than a month using by-product gases from steel plants in Tangjin. Using this technology, environmental pollutants will not be emitted by itself, and carbon monoxide in by-product gases can be fully utilized to reduce air pollution [68].



**Figure 1.40 Microbial hydrogen production process**

Recently, researchers from Henan Agricultural University plan to build an automated pilot-scale bioreactor system for dark fermentation and light fermentation (shown in Figure 1.41). By combining advanced technology with the bioreactor system, solar energy is used to provide heat, lighting and power to the system. An automatic control system was developed to monitor and regulate hot water, lighting, power and feed. During the 90 days of operation of the system, manual measurement methods were used to measure the basic process parameters, and then they were compared with the corresponding automatic measurements to determine the accuracy of the developed automatic control system [69].

In this experiment, a self-designed  $4 \text{ m}^3$  baffle-type photo-fermentation



hydrogen production reactor was used to study the effect of substrate concentration on photo-fermentation hydrogen production. The thesis studied the relationship between the parameters in the process of photo-fermentation biological hydrogen production, such as hydrogen production rate, hydrogen concentration, pH value, redox potential, biomass concentration and reducing sugar concentration. In the #3 reaction chamber, when the substrate concentration is  $20 \text{ g}\cdot\text{L}^{-1}$ , the highest hydrogen production rate is  $202.64\pm 8.83 \text{ mol}\cdot(\text{m}^3\cdot\text{d})^{-1}$ , and the hydrogen content is  $42.19\pm 0.94\%$  To  $49.71\pm 0.27\%$ . When the organic loading rate increases from  $3.3$  to  $20 \text{ g}\cdot(\text{L}\cdot\text{d})^{-1}$ , the hydrogen production rate increases, and then when the organic loading rate further increases to  $25 \text{ g}\cdot(\text{L}\cdot\text{d})^{-1}$ , the hydrogen production rate begins to decrease. In the continuous biological hydrogen production process, when the organic loading rate is maintained at  $20 \text{ g}\cdot(\text{L}\cdot\text{d})^{-1}$ , the maximum hydrogen production rate is  $148.65\pm 4.19 \text{ mol}\cdot(\text{m}^3\cdot\text{d})^{-1}$ .

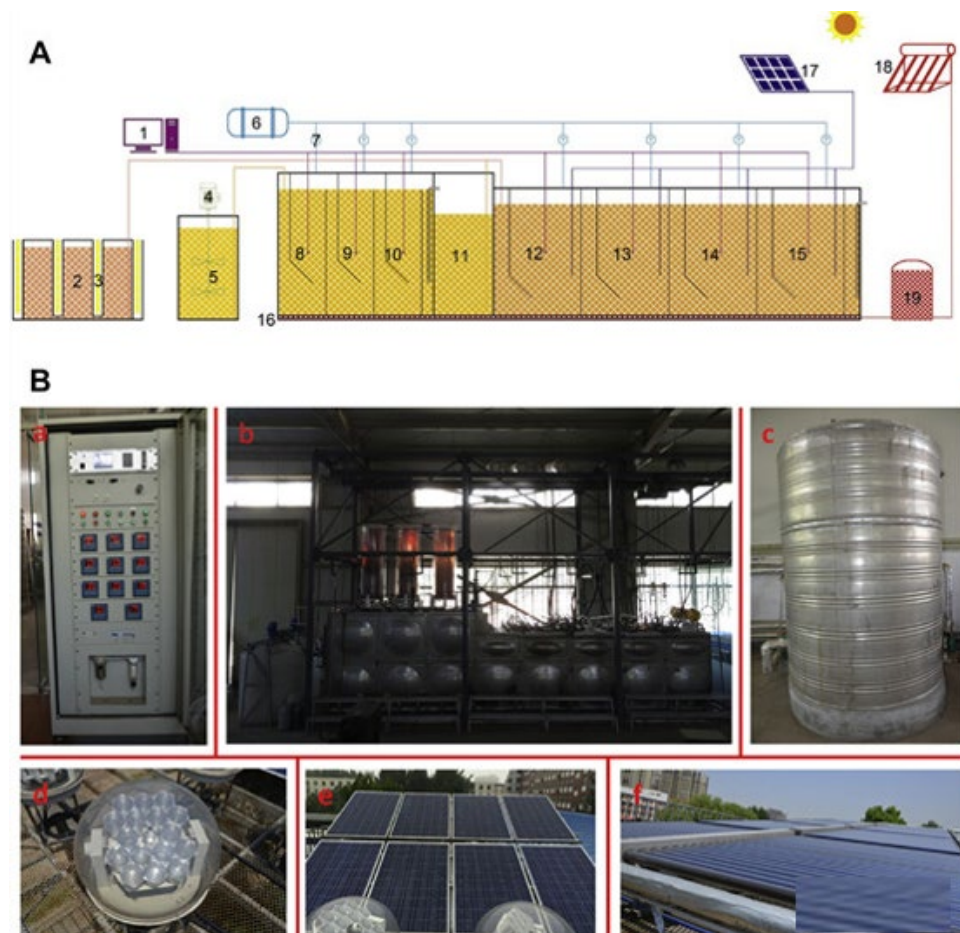
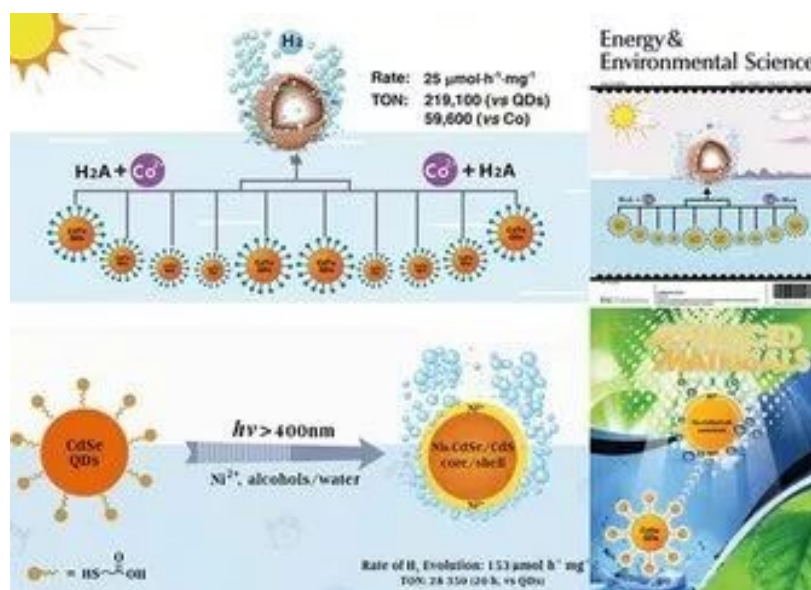


Figure 1.41 Main components of the bioreactor developed by Henan Agricultural University

The research team of biohydrogen production in the School of Municipal Environmental Engineering of Harbin Institute of Technology, using microbial electrolysis cell technology, realized biohydrogen production at 4°C through a cold-resistant electricity-producing bacteria existing in domestic sewage, thus overcoming the problem of low-temperature hydrogen production (Figure 1.42). This also provides a choice path for realizing the self-sufficiency of household energy. The energy conversion efficiency of this technology is high, only a small voltage (0.2-0.6V) can be provided to the circuit to overcome the thermodynamic barriers to produce hydrogen, while the traditional water electrolysis hydrogen production requires 1.8-2.0V voltage. If the energy of the substrate is not taken into account, this characteristic of the microbial electrolysis cell makes the hydrogen energy produced by the microbial electrolysis cell much larger than the energy input. Furthermore, microbial electrolysis cell technology can alleviate the organic pollution of water to some extent. Electrogenic bacteria can completely degrade most organic matters without producing new wastes [70].



**Figure 1.42 Schematic diagram of the use of microbial electrolytic cell technology proposed by Harbin Institute of Technology**

Lu et al. [71] used damaged apples in agricultural production as the raw material for the cultivation of photosynthetic bacteria HAU-M1 to explore the feasibility of this type of biological hydrogen production. The experiment discussed the influence of factors such as the initial pH value of the culture medium, light intensity, culture temperature, and the solid-liquid ratio of the culture medium, and the response surface method was used to optimize the

experiment. The results showed that when the initial pH of the culture solution was 7.14, the light intensity was 3029.67 Lx, the temperature was 30.46°C, and the solid-liquid ratio was 0.21, the maximum hydrogen yield was  $(111.85 \pm 1)$  mL·g<sup>-1</sup> raw material.

Jehlee et al. [72] used *Chlorella* sp. to produce hydrogen by two-step solid-state anaerobic fermentation at an appropriate temperature. When fresh *Chlorella* sp. is used, the output of hydrogen and methane can reach 124.9 and 230.1 mL·g<sup>-1</sup> VS, respectively, and the conversion efficiency of the matrix is 34%. When *Chlorella* sp. is pretreated at an appropriate temperature, the hydrogen and methane output of solid-state fermentation can be increased to 190.0 and 319.8 mL·g<sup>-1</sup> VS, respectively, and the substrate conversion rate is 47%.

Sattar et al. [73] used rice waste (rice straw, rice bran, etc.) to produce hydrogen by fermentation. Studies have shown that increasing the fermentation temperature can increase the amount of hydrogen produced by a variety of raw materials. Under the most suitable reaction temperature, the hydrogen production from rice straw is the highest, which can reach 40.04 mL·V<sup>-1</sup> Srem. When a variety of raw materials are jointly fermented to produce hydrogen, the amount of hydrogen produced can reach 30.37 mL·V<sup>-1</sup> Srem at a relatively moderate temperature. Experiments have proved that adjusting the fermentation pH between 6 and 7 will not adversely affect hydrogen production.

Kumar et al. [74] used dilute hydrochloric acid to pre-treat the biomass raw materials to obtain a pretreatment solution with a biomass content of 100 g·L<sup>-1</sup>, and use this as a substrate for hydrogen production research. Experiments have proved that microorganisms can be recycled. In the 10 cycles, the average cumulative hydrogen production volume can reach 770 mL·L<sup>-1</sup> pretreatment solution. When the hydraulic retention time is 16 h, the peak value of hydrogen production rate is 0.9 L·(L·d)<sup>-1</sup>, and the hydrogen yield is 86 mL·g<sup>-1</sup> at this time. Through the analysis of the microbial communities involved in the experiment, it was found that *Clostridium* had a promoting effect on the fermentation of hydrogen production.

Zagrodnik et al. [75] used starch as a raw material to use light-dark coupling fermentation to produce hydrogen by adding flow culture. In the dark fermentation stage, the pH value > 6.5 will generate acetic acid and lactic acid,

thereby reducing the hydrogen yield. Under suitable culture conditions, the feed rate is set to  $1.5 \text{ g starch} \cdot (\text{L} \cdot \text{d})^{-1}$ . After 11 days of continuous culture, the hydrogen yield is 3.23 L substrate, and the output is simple dark fermentation Twice the yield under the conditions. When the feed amount is  $0.375 \text{ g starch} \cdot (\text{L} \cdot \text{d})^{-1}$ , the starch conversion rate is the highest.。

At present, some large-scale production of hydrogen has been realized by thermochemical conversion, but the yield of hydrogen is not high <sup>[76]</sup>. Liquid-phase catalytic reforming for hydrogen production is based on biomass depolymerization, which has the advantages of easy concentration and transportation of depolymerization products, and is more suitable for large-scale hydrogen production. However, the technology is more complex and needs to be strengthened. Thermochemical hydrogen production is currently limited to Ni or noble metal catalysts, and the development of catalysts with high activity, long life and low cost is still the focus of research. In order to improve the yield of hydrogen, a variety of technologies can be combined. Firstly, thermochemical conversion of biomass is carried out, and then the products are reasonably distributed. The products with low commercial value are extracted and reformed, and the products with high commercial value are extracted and utilized <sup>[77]</sup>.

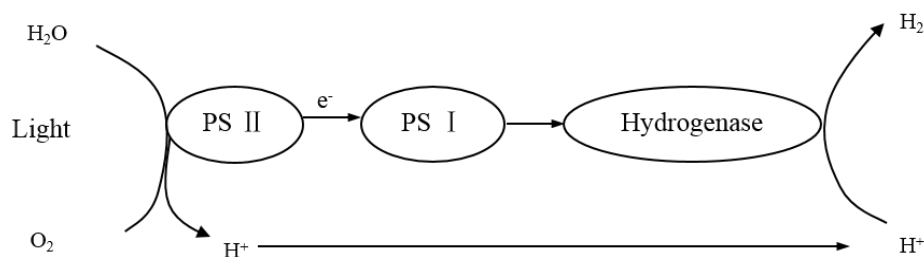
In the field of biological hydrogen production, there are also some problems that restrict its industrial development <sup>[78]</sup>: (1) Although the dark fermentation hydrogen production is stable and rapid, the accumulation of volatile acid will produce feedback inhibition, which limits the production of hydrogen. (2) In the production of hydrogen by microbial photolysis of water, low light energy conversion efficiency is the main limiting factor. Relying on genetic engineering methods, it is of great significance to obtain hydrogen-producing strains with higher light energy conversion efficiency through modification or mutagenesis. (3) In light-dark coupling fermentation for hydrogen production, the two types of bacteria have huge differences in growth rate and acid tolerance. The dark fermentation process has a fast acid production rate, which promotes the decrease of the pH value of the system, thereby inhibiting the growth of hydrogen production bacteria by light fermentation and reducing the overall hydrogen production efficiency. How to release the inhibition of the products between the two types of bacteria and achieve mutually beneficial symbiosis is an urgent

problem to be solved. In addition, cost issues also restrict the industrial application of hydrogen production technology, and the development and utilization of cheaper biomass raw materials can play a certain role in reducing the cost of hydrogen production.

### 4.3 Introduction to other biological hydrogen production methods

#### 4.3.1 Hydrogen production by photolysis of water

Microorganisms decompose water into produce hydrogen by photosynthesis. Currently, photosynthetic bacteria and blue-green algae are mostly studied. Take blue-green algae as an example. They decompose water through photosynthesis to produce  $O_2$  and  $H_2$  under anaerobic conditions. The process is shown in the figure. There are two independent and coordinated systems in photosynthesis: ① Photosystem II (PS II) that receives light energy to split water to produce  $H^+$ ,  $e^-$  and  $O_2$ ; ②Photosystem I that produces reducing agent to fix  $CO_2$  (PS I). The electrons generated by PS II are carried by ferredoxin to the hydrogenase through PS II and PS I, and  $H^+$  is catalyzed by the hydrogenase to generate  $H_2$  [79].



**Figure 1.43 Schematic diagram of the photosynthetic hydrogen production process of blue-green algae**

Hydrogen production by photosynthetic bacteria is the result of photosynthesis as cyanobacteria, but photosynthetic bacteria have only one photosynthetic center (equivalent to the PS I of cyanobacteria). Due to the lack of PS II which plays a role in photolysis of algae, only non-oxygen photosynthesis with organic matter as electron donor is carried out.

### 4.3.2 Light and dark coupling fermentation for hydrogen production

Using the respective advantages and complementary characteristics of anaerobic photo-fermentation hydrogen-producing bacteria and dark-fermentation hydrogen-producing bacteria, a new mode of combining the two to improve hydrogen production capacity and substrate conversion efficiency is called light-dark coupling fermentation hydrogen production. Hydrogen-producing bacteria by dark fermentation can decompose macromolecular organic matter into small molecular organic acids to obtain the energy and reducing power needed to maintain their own growth, and release hydrogen. Due to the organic acids produced by dark fermentation bacteria can not continue to use and large accumulation, resulting in low efficiency of hydrogen production by dark fermentation bacteria. Light fermentation hydrogen-producing bacteria can utilize small molecular organic acids produced by dark fermentation to eliminate the inhibition of organic acids on dark fermentation and further release hydrogen. Therefore, coupling the two can improve the efficiency of hydrogen production and expand the scope of substrate application.

Taking glucose as an example, coupled fermentation reactions are shown in the equation.

Dark fermentation stage:  $\text{C}_6\text{H}_{12}\text{O}_6 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + 2\text{CO}_2 + 2\text{CH}_3\text{COOH}$

Light fermentation stage:  $2\text{CH}_3\text{COOH} + 4\text{H}_2\text{O} + \text{light energy} \rightarrow 8\text{H}_2 + 4\text{CO}_2$

Table 1.14 shows the hydrogen production by light-dark coupling fermentation under different substrate conditions<sup>[80]</sup>. Figure 1.15 shows the direct fermentation of various cellulose substrates to produce hydrogen<sup>[81]</sup>.

**Table 1.14 Hydrogen production by light-dark coupling fermentation under different substrate conditions**

Matrix type	Dark fermenting bacteria	Light fermentation	Hydrogen yield (mol·mol <sup>-1</sup> )
<b>GLUCOSE</b>	Ethanoligenensharbinense B49	Rhodopseudomonas faecalis RLD-53	6.32
<b>SUCROSE</b>	Clostridium pasteurianum	Rhodopseudomonas palustris WP3-5	7.10
<b>CASSAVA</b>	Microflora	Rhodobactersphacroides ZX-5	6.51
<b>STARCH</b>			
<b>FOOD</b>	Microflora	Rhodobactersphacroides ZX-5	5.40
<b>WASTE</b>			

<b>MISCANT HUS SUCROSE</b>	Thermotogancapolutana C.soccharolyticus	Rhodobactercapsulatus R. capsulatus	4.50 13.7
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**Table 1.15 Hydrogen production by direct fermentation of cellulosic substrates**

<b>CELLULOSE MATRIX</b>	microorganism	temperature (°C)	Hydrogen yield
<b>CELLULOSE MN301</b>	Clostridium cellulolyticum	37	1.7(mol·mol <sup>-1</sup> ) glucose
<b>MICROCRYSTAL LINE CELLULOSE CELLULOSE MN301</b>	Clostridium cellulolyticum	37	1.7(mol·mol <sup>-1</sup> ) glucose
<b>MICROCRYSTAL LINE CELLULOSE DELIGNIFIED CELLULOSE BAGASSE</b>	Clostridium populeti	37	1.(mol·mol <sup>-1</sup> ) glucose
<b>WHEAT STRAW</b>	Clostridium populeti	37	1.4(mol·mol <sup>-1</sup> ) glucose
<b>CORN STALK LEAVES</b>	Clostridium thermellum ATCC 27045	60	1.6(mol·mol <sup>-1</sup> ) glucose
	Caldicellulosiruptorsaccharolyticus	70	19.21(mL·g <sup>-1</sup> ) raw material
	Caldicellulosiruptorsaccharolyticus	70	44.89(mL·g <sup>-1</sup> ) raw material
	Caldicellulosiruptorsaccharolyticus	70	38.14(mL·g <sup>-1</sup> ) raw material

The results show that screening more efficient strains was very important for hydrogen production by light-dark coupling fermentation, so more scientific research was also essential.。

## **5. New hydrogen production method**

This part mainly introduces some potential hydrogen production methods. It should be noted that the methods involved in this part are not necessarily industrialized, but are intended to propose a hydrogen production method for reference.

### **5.1 Plasma hydrogen production**

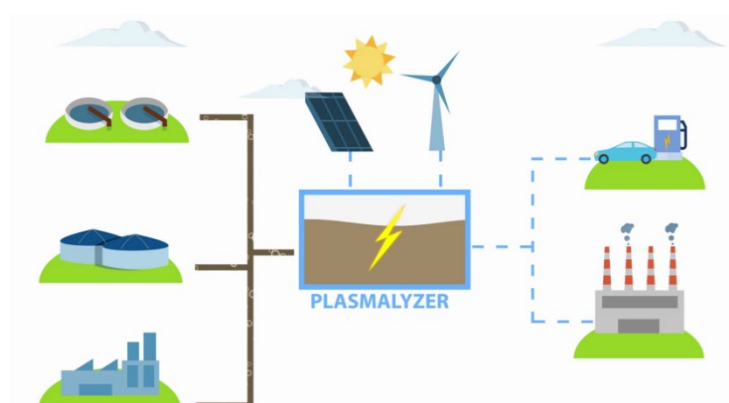
Objects in nature mainly exist in three forms: gas, liquid and solid. Generally speaking, when the external heat source continues to supply energy to the solid material to reach the solubility point, the molecular polymerization force between the material decreases, and the material is transformed from solid to liquid. If the heat source continues to supply, the molecular polymerization force between the liquid material continues to decrease, and when the boiling point is reached, the material gradually transforms from liquid to gas. If we continue to provide energy on the gaseous material basis to a certain extent, some atoms and molecules can be ionized. When the temperature continues to be higher than the temperature, most of the substances will be in the state of ionization, then the material will appear the fourth state, namely plasma. Plasma mainly contains molecules, positive and negative ions, atoms, electrons and photons. The whole plasma is electrically neutral and is a good conductor.

Liquid-phase plasma hydrogen production technology is an emerging hydrogen production technology. Since the liquid phase discharge used in the hydrogen production method generates plasma and has high mass transfer efficiency, the hydrogen production effect is good, the hydrogen production is large, and the hydrogen production energy consumption is low. The plasma hydrogen production method can produce hydrogen from various hydrogen-containing raw materials, with a wide range of raw materials selection (see Figure 1.44 for the process). This method avoids excessive dependence on non-renewable energy sources such as fossil fuels, and instead chooses renewable energy sources such as ethanol and water. And when other hydrocarbons are used as raw materials to produce hydrogen, the plasma method can improve the flexibility and variability of the system, especially in vehicle-mounted hydrogen



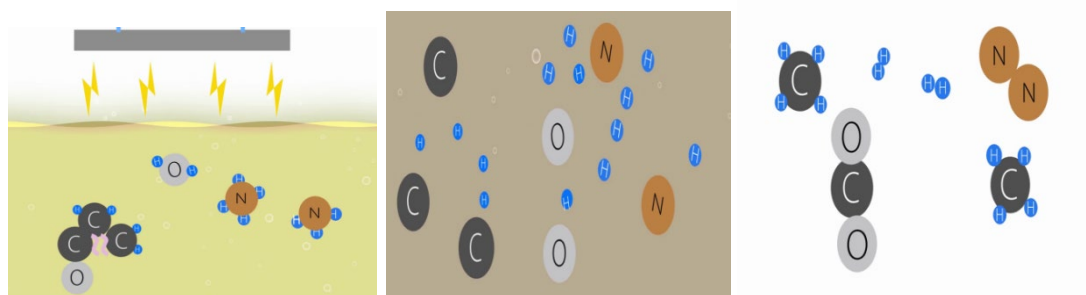
production [82].

Sewage treatment, biogas or wastewater from industrial plants contain nitrogen and organic carbon compounds. These compounds can be used to produce valuable renewable fuels instead of just spending huge costs and energy costs and expenses for cleaning. The use of wind energy and solar energy to upgrade technology utilization, and the use of renewable energy to generate plasma, this technology is called plasma decomposition (Plasmalysis).



**Figure 1.44 Schematic diagram of plasma production of hydrogen**

Renewable energy is used to produce plasma, which breaks the chemical bonds of nitrogen and carbon compounds in wastewater. The atoms are recombined in the plasma field, releasing gas, leaving purified water. The released hydrogen, methane, nitrogen and carbon dioxide are fed into the gas separation membrane to separate hydrogen from other target gases (Figure 1.45).



**Figure 1.45 Schematic diagram of organic bond breaking and gas bonding**

The advantages of plasma include: (1) The organic matter in sewage has a high degree of ionization and decomposition; (2) The ratio of electron temperature and ion temperature to neutral gas temperature is very high, and the carrier gas can maintain a suitable temperature. This feature makes the temperature of the substrate not too high in the case of vapor deposition; (3) It

can maintain the plasma under high pressure; (4) There is no internal electrode in the case of gas discharge, and there is no working gas in the plasma container. Therefore, it is clean and free of pollution sources. The plasma generator can maintain a long life; (5) The plasma can be confined in the agreed space by the magnetic confinement method, which has a certain degree of safety.

The plasma hydrogen production method has excellent performance in both hydrogen production and energy consumption, and has certain application prospects. However, the plasma hydrogen production technology is still in the research stage, and it is urgent to accelerate the application of this research. The first thing to do is to ensure that it reaches a certain energy efficiency. According to the analysis of the US Department of Energy, the goal of hydrogen production technology by 2020 is to meet the energy efficiency of hydrogen production not less than  $60\text{gH}_2 \cdot \text{kWh}^{-1}$  (about  $1.5 \text{ US dollars} \cdot (\text{kgH}_2)^{-1}$ ). At present, there are only a few forms of hydrogen production that can meet this standard, but the amount of hydrogen production is very low and it is difficult to apply. Due to the short development history of plasma hydrogen production, there are few optimization methods available, and the optimization of equipment is an important step in the road to practical application of this technology.

At present, the German company Graforce has developed a technology that uses a plasma method coupled with solar power to treat sewage to prepare hydrogen and biogas. The basic process and product separation principles are shown in Figures 1.46 and 1.47.

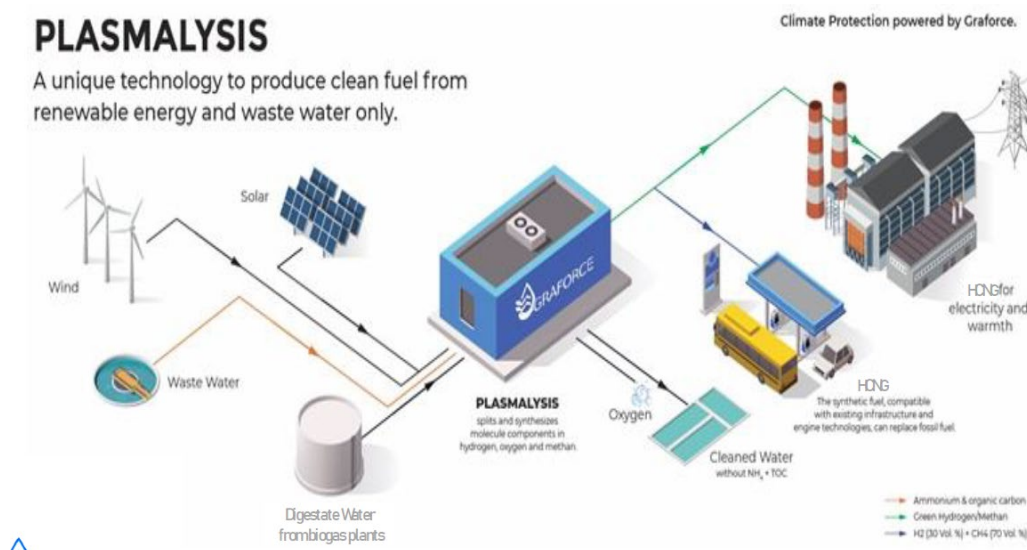


Figure 1.46 The basic process flow of plasma wastewater hydrogen production

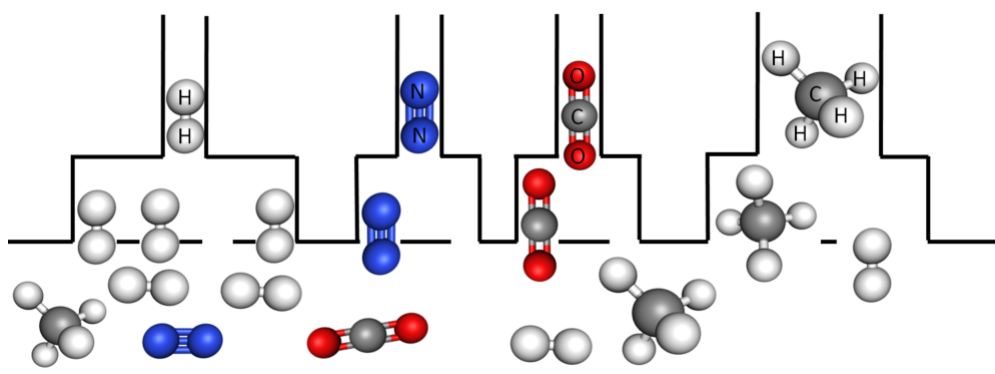


Figure 1.47 The principle of product separation developed by Geforce

This technology uses solar panels to generate electricity and produces electricity for plasma power. The generated plasma is used to decompose organic matter in sewage to produce hydrogen and other biogas, and further achieve effective separation of hydrogen through membrane separation.

## 5.2 Laser hydrogen production

Laser hydrogen production is essentially a special case of plasma hydrogen production. Its principle and basic equipment are shown in Figure 1.48. The principle is that water molecules generate water free radicals under the action of the laser, which are further dissociated into hydrogen free radicals and hydroxide free radicals. Some hydrogen radicals and hydroxyl radicals produce water. On

the other hand, hydrogen radicals can polymerize themselves to produce hydrogen, and hydrogen peroxide is produced as a by-product in this process. However, studies have found that only water within the laser beam can be plasmaized, so the efficiency of the hydrogen production method is relatively low. In addition, in terms of hydrogen production efficiency, the laser hydrogen production is  $0.4 \text{ g H}_2 \cdot (\text{kWh})^{-1}$ , while the traditional photocatalytic water splitting hydrogen production is  $0.01 \text{ g H}_2 \cdot (\text{kWh})^{-1}$ , corona discharge and other three-dimensional bodies The method hydrogen production is  $2 \text{ g H}_2 \cdot (\text{kWh})^{-1}$ , and the sliding arc discharge plasma hydrogen production is  $1.3 \text{ g H}_2 \cdot (\text{kWh})^{-1}$ , which indicates that the technology has room for further research.。

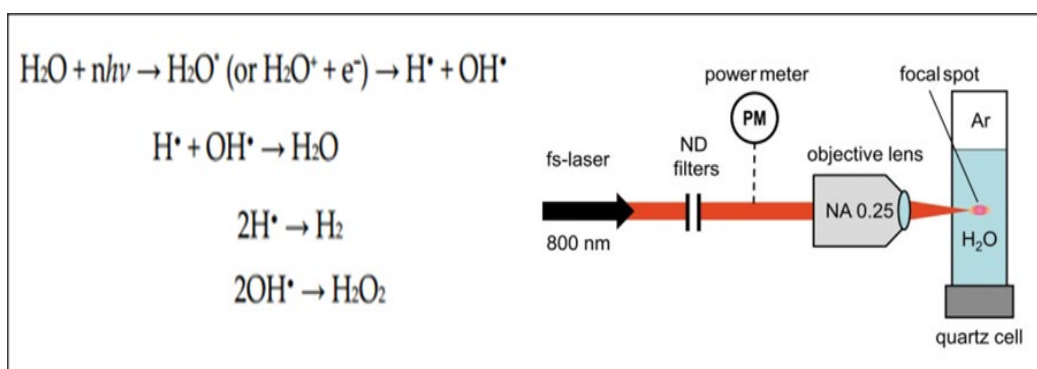


Figure 1.48 Principle and device diagram of laser hydrogen production

### 5.3 Photocatalytic hydrogen production

The hydrogen production system using solar energy is specifically composed of hydrogen production system with light decomposition, solar power generation and electrolysis water. Since Fujishima and Honda realized photocatalytic hydrogen production on  $\text{TiO}_2$  single crystal electrode in 1972, photocatalytic water splitting technology has been the focus of attention of scientists. Compared with traditional hydrogen production by electrolysis of water and hydrogen production by pyrolysis of fossil energy, photocatalytic hydrogen production by decomposition of water can make use of abundant solar energy and water to produce hydrogen, which effectively avoids the shortcomings of high energy consumption and large pollution caused by traditional technology. Therefore, it is considered to be the most ideal way to develop hydrogen energy [83].

The semiconductor photocatalysis process is usually divided into three main stages [84]: (1) The semiconductor absorbs photons with energy greater than the

band gap to generate electron-hole pairs; (2) the photo-generated electron-hole pairs separate and migrate to the surface of the material (3) The photogenerated holes and electrons that migrate to the surface of the material undergo redox reactions with the adsorbed species respectively.

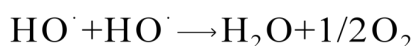
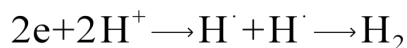
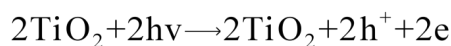


Figure 1.49 shows the process reaction of nano-TiO<sub>2</sub> photocatalytic water splitting [85]. Photocatalytic decomposition of water to produce hydrogen is an energy conversion process that converts light energy into chemical energy. Among them, semiconductor photocatalysts play a vital role. As shown in the figure, when the semiconductor is irradiated with light whose photon energy is equal to or higher than the forbidden band width of the semiconductor, the valence band electrons of the semiconductor will transition to the conduction band, and holes are generated at the valence band position. When the photo-generated holes and electrons migrate to the surface of the photocatalyst, they will undergo redox reactions with substances adsorbed on the surface of the catalyst under appropriate conditions [86]. In the photocatalytic decomposition of water to produce hydrogen system, the electrons that migrate to the surface of the catalyst can reduce H<sup>+</sup> and release hydrogen. .

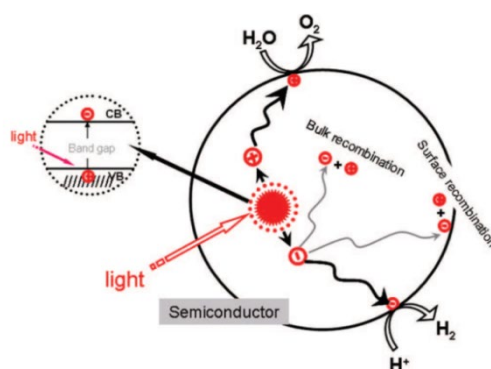


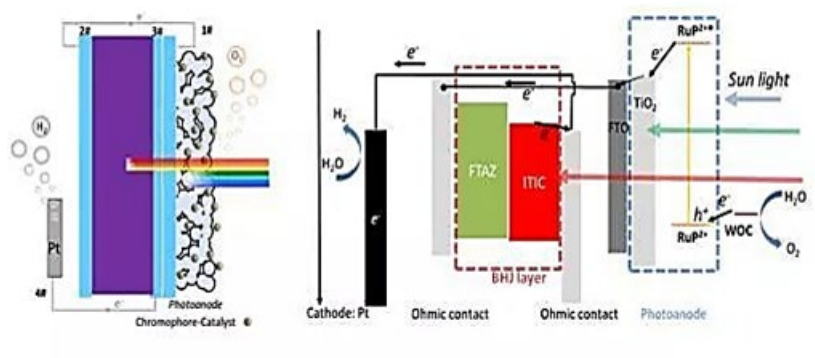
Figure 1.49 Principle of photocatalytic water splitting [87]

Semiconductor photocatalytic hydrogen production can not only use clean and renewable solar energy to produce efficient and clean hydrogen energy, but

also effectively reduce CO<sub>2</sub> emissions and alleviate environmental pollution problems. In addition, semiconductor photocatalysis or photoelectrocatalysis requires simple equipment and mild reaction conditions. It is the most attractive hydrogen production method and one of the most promising technologies for industrial applications [88].

Modifying the promoter on the photocatalyst surface can promote the separation of photogenerated electrons and holes to a certain extent, reduce the overpotential of hydrogen production, and thereby improve the hydrogen production efficiency of the photocatalyst. The current development trends of promoters in photocatalytic hydrogen production systems are as follows: (1) Development from noble metal promoters to transition metal compound promoters; (2) Development from single promoters to multi-element promoters, in order to achieve full water under sunlight break down. In the above aspects, researchers have made considerable progress, but the matching relationship between the promoter and the photocatalyst, the design of the composition and structure of the promoter, and other issues still need to be studied in depth [89].

The Institute of Ningbo Institute of Materials, Chinese Academy of Sciences added a dye-sensitized photoelectric synthesis cell (DSPEC) to an organic light-absorbing group to convert water into O<sub>2</sub> and H<sub>2</sub> using visible light (Figure 1.50). The experimental results show that the conversion efficiency of solar energy to hydrogen energy of the visible light absorbing electrode is greatly improved, and provides a benchmark for the conversion efficiency of molecular-based solar fuels. Combining the DSPEC photoanode with the organic solar cell OSC, the efficiency of solar artificial water splitting to produce hydrogen is as high as 1.5%, while the efficiency of natural photosynthesis is only 1.0% [90].



**Figure 1.50 Schematic diagram of the working principle of dye-sensitized photoelectric synthesis cell (DSPEC)**

## **5.4 Calcium hydroxide reacts with water**

Calcium hydroxide mixed with water can produce hydrogen and calcium hydroxide. Calcium hydroxide, also known as lime, is a neutralizer for acidic river water and soil, as well as a safe substance in food coagulants. Since the instantaneous contact of calcium hydride powder with water will produce strong chemical reactions and generate hydrogen explosively, it cannot be directly used in hydrogen fuel cells in the past. Recently, Roma Co., Ltd. used a special resin to solidify the original powdered calcium hydroxide into flake <sup>[91]</sup>, reducing the reaction rate to a few thousandth of the original, and successfully developed a safe and stable solid hydrogen fuel source that can produce hydrogen on demand. In addition, Roma Co., Ltd. also developed small components for efficient generation of hydrogen and semiconductor technology for stable supply of electricity, which provided more possibilities for hydrogen production.

## 6. Comparison of common hydrogen production methods

At present, the technology of hydrogen production in industry has been very mature. Hydrogen production from fossil fuels, hydrogen production from chemical by-products, hydrogen production from water electrolysis and hydrogen production from methanol have been used in commerce. Photoelectrochemical and biohydrogen production are still in the stage of technological development. In terms of the operation of hydrogenation stations in China and abroad, the current hydrogen supply methods are mainly divided into two types: in-station hydrogen production and external hydrogen supply. The in-station hydrogen production is mainly water electrolysis, the technology has been quite mature and has been used in most European hydrogenation stations. External hydrogen is a large-scale use of natural gas reforming to produce hydrogen or by-product hydrogen from steel plants and chemical plants, and after purification, it is transported to the hydrogenation station by high pressure oxygen cylinder cluster trailer (Figure 1.51).

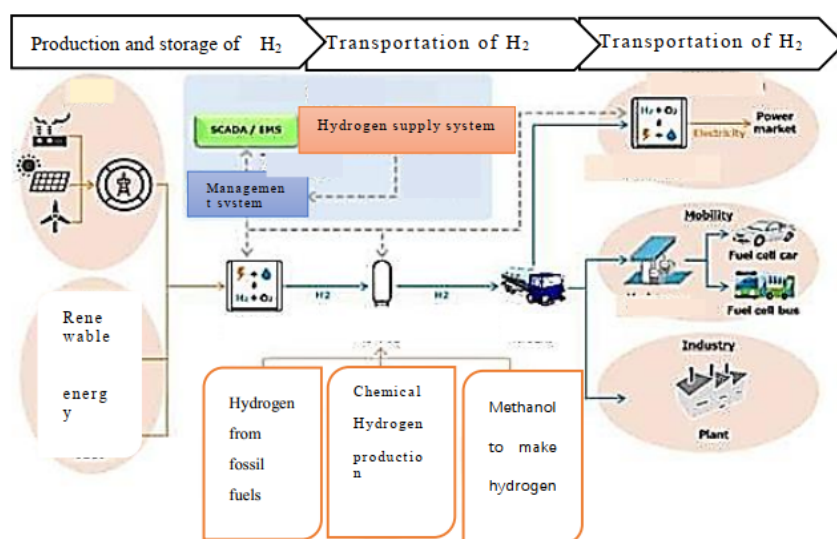


Figure 1.51 Schematic diagram of the current hydrogen industry chain

The domestic hydrogen energy reserves for external hydrogen supply are very sufficient, but the downstream hydrogen supply system is still in the



embryonic stage of exploration, and the economic performance of several hydrogen production routes needs to be verified. Looking forward to the future, due to the strict control of the total coal index in the eastern region of China where the load center is concentrated, and the supply of natural gas is relatively tight in the medium term, the feasibility of hydrogen production from fossil fuels (coal to hydrogen and natural gas reforming to hydrogen) as a directional hydrogen supply route is difficult to be popularized on a large scale before being confirmed. Although the water electrolysis route can achieve decentralized hydrogen supply, its cost depends on whether the power cost decreases. The level of power curtailment utilization of domestic wind power and photovoltaic is the key to the development of the route in the future.

From the current view, the utilization mode of by-product hydrogen in domestic chemical industry is the best choice for hydrogen supply in fuel cell industry. Domestic chlor-alkali, PDH and rapid development of ethane cracking industry can provide sufficient low-cost hydrogen resources, and focus on the East China area with dense load centers. After low-intensity transformation, the problem of hydrogen supply and efficient utilization of by-product hydrogen in fuel cell industry can be solved at the same time. In the future, centralized hydrogen supply and decentralized hydrogen production by water electrolysis will be the main development trend of hydrogen supply mode in domestic fuel cell industry.

The main hydrogen production methods include input raw materials, energy sources, characteristics and technologies, and various hydrogen production methods. The technical indicators are shown in Table 1.16 and Table 1.17. Common hydrogen production technologies include hydrogen production from coal, hydrogen production from natural gas and petroleum, and hydrogen production from industrial by-products. Among them, the technology of hydrogen production by electrolysis of water is relatively mature, and some technologies have entered the practical stage. In the electrolysis of water hydrogen technology, electricity price is the decisive factor.

**Table 1.16 Comparison of technical characteristics of main hydrogen production methods** <sup>[12]</sup>

Hydrogen production from fossil fuels	Coal, oil, natural gas, etc.	heat	Inexpensive, emissions CO <sub>2</sub>	Practical stage
Industrial by-product hydrogen	Chlor-alkali, coke oven gas, etc	Heat/electricity	cheap	Practical stage
Alkaline water electrolysis			Existing technology	Practical stage
Proton exchange membrane water electrolysis			Can increase current density	Verification phase
Water electrolysis	water	Electricity (partial heat)	Electricity comes from renewable energy sources, no CO <sub>2</sub> emissions	Water vapor decomposes at high temperature, seeking to supplement the necessary electric energy for water electrolysis with heat
high temperature electrolysis of steam				development stage
Bioenergy fermentation	Bioenergy	Heat, electricity	Utilize biomass energy, alkali neutrality	Part of the practical stage
Thermochemical method	water	heat	Utilize the chemical reaction of iodine and sulfide to	development stage

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Comparison of common hydrogen production methods

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Photocatalytic	water	light	improve energy conversion efficiency The necessary energy is close to sunlight, and the energy conversion efficiency is low	Research phase
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Table 1.17 List of indicators of main hydrogen production methods <sup>[93]</sup>

Hydrogen production process	Gas hydrogen production	Hydrogen production from natural gas	Ammonia decomposition for hydrogen production	Hydrogen production by water electrolysis	Methanol cracking for hydrogen production
Use scale	1000-2000M <sup>3</sup>	>5000M <sup>3</sup>	<50M <sup>3</sup>	2-300M <sup>3</sup>	<20000M <sup>3</sup>
Hydrogen production cost (yuan·Nm <sup>-3</sup> )	0.6-1.2	0.8-1.5	2-2.5	2.5-3.5	1.8-2.5
Operating parameters	Reaction pressure≈0.7MPA	Reaction pressure>1.5MPA	Working pressure 0.05MPA, temperature 800-850°C	The working pressure of the electrolyzer can reach 4.0MPA, and the temperature of the outgoing gas is ≈90°C	Working pressure 102 MPA, temperature 260-290°C
Technical index	Purity ≥99%, by-product CO <sub>2</sub>	The purity is 39-59%, CO <sub>2</sub> , CO and CH <sub>4</sub> can be recovered, and the hydrogen recovery rate is 70%	The maximum output is 200m <sup>3</sup> ·h <sup>-1</sup> , the highest purity is 39-49%, and the comprehensive gas N <sub>2</sub> can be recovered	The maximum output is 300m <sup>3</sup> ·h <sup>-1</sup> , the maximum purity is 69%, and oxygen can be recovered	The maximum output is 20000M <sup>3</sup> ·H <sup>-1</sup> , the purity is 39-79%, carbon monoxide and carbon dioxide can be recovered

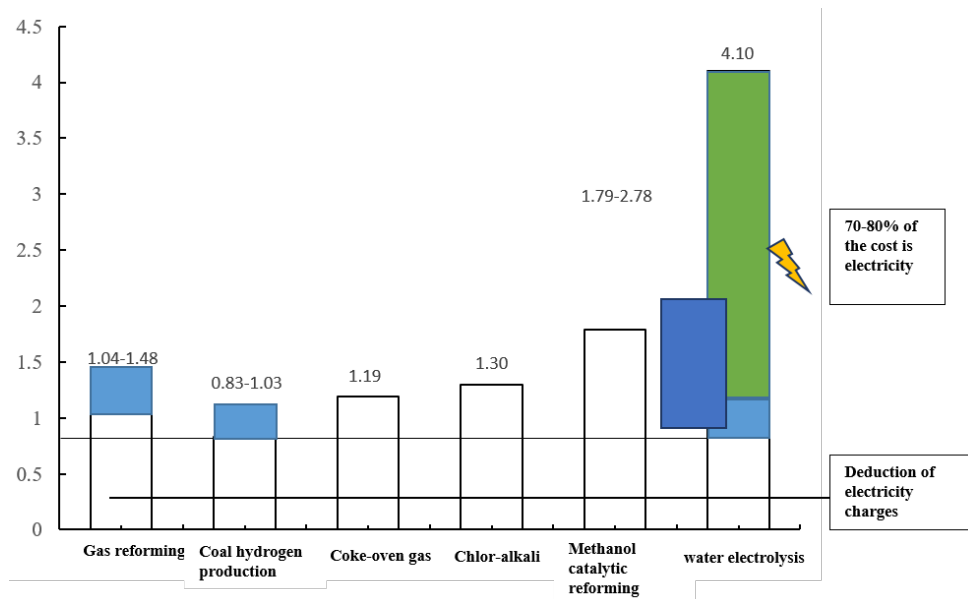
Main consumption (/Nm <sup>3</sup> )	coal: 7.3kg Electricity: 0.355kw·h <sup>-1</sup>	Raw material natural gas 0.48m fuel natural gas 0.12m <sup>3</sup> boiler water supply 1.7kg, power supply 0.2kw·h <sup>-1</sup>	Electricity 1.3kw·h <sup>-1</sup> Liquid nitrogen 0.52kg·M <sup>-3</sup>	Desalted water 0.82kg, Electricity 505kw·h <sup>-1</sup>	Electricity 0.0556kw·h <sup>-1</sup> , Methanol 0.52kg
Technology, environmental protection and safety	The process time is long, the manufacturing environment is poor, and it is easy to pollute the environment	Discharge a small amount of boiler sewage, CO <sub>2</sub> and steam, and a small amount of spent catalyst	1. The reactor is resistant to high temperature; the reactor converter material is stable and consumes a lot of electricity; 2. The storage and transportation of liquid ammonia must use a pressure vessel of more than 30kg; 3. Ammonia gas is easy to explode; 4. Liquid ammonia is toxic	Simple process, stable work, fully automatic operation	Methanol is suitable for environmental protection, safe transportation and cost saving

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Land area	100m*80m	50m*30m (limited to the supply of natural gas)	20m*15m, liquid ammonia is supplied near the factory	50m*20m, liquid ammonia is supplied near the factory	20m*15m, methanol supply is near the factory
Advantage areas	Medium and large- scale hydrogen production plant	Mass production process	Medium to high requirements, small to medium scale	Small scale, requiring high-end precision	Medium to high requirements, medium to large scale

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Cost is an important indicator of whether hydrogen production methods are widely used. Figure 1.52 lists the economic comparison of important hydrogen production methods. It can be concluded that the main cost of hydrogen production from electrolytic water is the electricity cost, and the cost of electricity determines the cost of hydrogen. The hydrogen production process from electrolytic water needs to reduce the electricity cost as much as possible.



**Figure 1.52 Technical and economic comparison of main hydrogen production methods** <sup>[12]</sup>

Evaluate the hydrogen cost corresponding to different hydrogen production methods with different hydrogen transportation methods, and the results are shown in Figure 1.53.





By comparing and analyzing the cost and advantages and disadvantages of various hydrogen production methods, at this stage, the main route of by-product hydrogen production in chlor-alkali industry with low cost and high purity of hydrogen products is selected, which can meet the hydrogen demand for downstream battery vehicles. In the future, the development of hydrogen energy industry chain is more perfect, the use of renewable energy to produce hydrogen from electrolytic water will become the final solution of energy. The reasons are as follows: (1) The water gas method has the lowest cost of hydrogen production and a large scale of application, but the carbon dioxide emissions are the highest, and the generated hydrogen has a high sulfur content. If it is used in a fuel cell, it will cause the fuel cell catalyst to be poisoned; The hydrogen produced by it is processed, which not only adds extra cost, but also has high requirements on technical standards. (2) The cost of hydrogen production by steam reforming of petroleum and natural gas is second, about  $0.7\sim 1.6$  yuan $\cdot$ Nm $^{-3}$ , and the energy conversion rate is as high as 72%, but the environmental protection is not good. In the future, carbon capture technology can be considered to reduce carbon emission. (3) The cost of the chlor-alkali hydrogen production process is moderate, ranging from 1.3 to 1.5 yuan $\cdot$ Nm $^{-3}$ , and the environmental performance is good, and the hydrogen produced is of high purity. At present, it is suitable for large-scale production of hydrogen raw materials used in fuel cells, and it is also an important source of hydrogen. (4) The cost of methanol cracking and liquid ammonia cracking is about 50% higher than that of chlor-alkali hydrogen production. Compared with fossil resource hydrogen production technology, the initial investment and energy consumption are lower, and the unit hydrogen cost is lower than that of water electrolysis hydrogen production. (5) The cost of hydrogen production by water electrolysis is the highest, between 2.5~3.5 yuan $\cdot$ Nm $^{-3}$ , and the cost is continuously decreasing, the carbon emission is low, and the energy conversion rate is as high as 70% under the application of hydraulic, tidal, and wind energy. the above. Under the conditions of close integration with renewable energy in the future, hydrogen production by water electrolysis will become the mainstream route for hydrogen sources.

In addition, according to different hydrogen production processes, the carbon emissions are also different, and hydrogen can be divided into green hydrogen,

blue hydrogen and gray hydrogen. Since hydrogen production from renewable energy electrolysis water is cleaner and cheaper than that from network electrolysis water (Table 1.18), with the development of hydrogen storage and transportation technology, the cost of hydrogen production from renewable energy electrolysis water will continue to decline. The traditional hydrogen production method of petrochemical energy combined with CCS/CCUS technology can reduce carbon emissions, and the cost of hydrogen production is lower than that of hydrogen production from electrolytic water, which still has a large cost advantage. Hydrogen production from electrolytic water by renewable energy can effectively solve the problems of high cost and carbon emission.

**Table 1.18 Comparison of economics and carbon emissions of main hydrogen production processes <sup>[7]</sup>**

classification	Main technique	Hydrogen production cost (Yuan·kg <sup>-1</sup> )	carbon emission kg (H <sub>2</sub> )
Green hydrogen	Renewable energy electrolysis hydrogen production	19.4	
Blue hydrogen	Natural gas reforming to produce hydrogen +CCUS	16.1	
	Coal gasification hydrogen production +CCUS	10.1	
	Natural gas reforming to produce hydrogen	11.7	8.1
Gray hydrogen	Industrial by-product hydrogen 2+PSA	12.0	20.7
	Coal gasification hydrogen production	7.0	30.2
	Hydrogen production by grid electricity electrolysis of water	36.2	35.8

Due to the inhomogeneity and indirectness of renewable energy generation, grid fluctuation is easily caused by grid-connected transmission, so a large number of renewable energy sources are not used in grid-connected. In 2019, the average abandoned wind rate was 4.7% at  $1.69 \times 10^{10}$  kW. The average abandoned light rate is 2% at  $4.5 \times 10^9$  kW. Using “abandoned wind, abandoned light and abandoned water” power to produce hydrogen from water electrolysis has become a new idea for the development of green hydrogen energy. For example, the cost of hydrogen production can be reduced to about 10 yuan·kg<sup>-1</sup> according to 0.1 yuan·kWh<sup>-1</sup> of electricity abandonment, and the cost of hydrogen production is equivalent to that of traditional fossil fuel. And because of the green energy power generation, the carbon emission problem is basically solved. Therefore, the country and even around the world are promoting the development of renewable energy hydrogen production. In 2016, Hebei Construction and Investment New Energy Company drew lessons from the experience and practice of Germany Brandenburg in the development and utilization of renewable energy and improving the ecological environment, and cited the wind power hydrogen production technology of Germany McPhy Energy Company to plan and construct the “Guyuan wind power hydrogen production demonstration project”. In 2019, Zhangjiakou Haiperer hydrogen production and hydrogenation project was invested and constructed by Yihuatong Power Technology Co., Ltd., including a

hydrogen production station and a supporting hydrogenation station. The hydrogen production station uses the hydrogen production technology of wind power electrolysis water. After the project is completed, the annual yield of hydrogen with purity of 99.999% is  $1.6 \times 10^7 \text{m}^3$ . In addition, Sichuan, Guangdong and other places proposed electricity price support policy, the maximum electricity price of hydrogen production from electrolytic water is limited to  $0.3 \text{ yuan} \cdot \text{kWh}^{-1}$  and  $0.26 \text{ yuan} \cdot \text{kWh}^{-1}$ . However, since China's centralized large-scale wind power and photovoltaic power plants are mainly located in the northwest region, the hydrogen produced by power abandonment is transported to the eastern and southern regions of China, which is not only related to the high cost of hydrogen transportation but also includes safety and other issues. With the development of hydrogen storage and transportation technology and the construction of hydrogen transportation network, the cost of hydrogen production from renewable energy is expected to decrease further in the future.

Combined with China's specific national conditions, on the one hand, coupled with a variety of power generation mode of electrolytic water hydrogen production has great competitiveness. In addition, coal and petrochemical products still occupy the main hydrogen production market for a long time. At the same time, the future market will be a situation of coexistence of various hydrogen production methods. According to the characteristics of different regions, scientific selection of appropriate hydrogen production methods and enterprise models will have greater benefits. It is hoped that through the sincere cooperation of different industries and the strong support of the "14 th Five-Year" policy, the hydrogen industry in China will be pushed to a peak.

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# **Chapter 2 Carbon Emission Calculation and Benefit Analysis of Hydrogen Production Project by Electrolysis of Alkaline Water**

## **1. Background**

### **1.1 Development status of hydrogen energy**

With the continuous maturity of clean energy application technology and the continuous advancement of China's energy structure adjustment, the development momentum of the hydrogen industry continues to be good, and was first written in "Government Work Report" in 2019. Hydrogen is recognized as a clean energy and is emerging as a low-carbon and zero-carbon energy. At present, the scale of hydrogen energy industry continues to expand, China has become the world's largest hydrogen producer. China's current capacity for hydrogen production is 25 million tons/year, and hydrogen production is 20-22 million tons/year, accounting for one third of the world's hydrogen production, providing basic conditions for the early stage of industrialization of hydrogen energy development and its applications. In 2018, China's renewable energy abandoned nearly 100 billion kWh, making it possible to achieve large-scale, low-cost and green production of hydrogen.

The main technical routes of hydrogen production in China are coal gasification and industrial by-product hydrogen. Biological hydrogen production and electrolytic water hydrogen production account for a relatively low proportion in the industry due to high cost. The combination of hydrogen energy technology and renewable energy technology is the main direction of future development. The production of hydrogen promotes the overall operation of the entire hydrogen energy industry chain through the effective combination of hydrogen production and renewable energy power, so as to achieve zero emissions

in the use of hydrogen energy and effectively expand the secondary utilization of renewable energy.

The development of China's hydrogen energy industry still faces many problems. In addition to the technical bottlenecks related to the production, transfer and utilization of hydrogen energy, it is also reflected in the following aspects:

1. Hydrogen production mainly relies on fossil fuels. From the perspective of the whole life cycle, the effect of carbon emission reduction is not obvious. Hydrogen produced from fossil fuels such as coal, natural gas, and petroleum accounts for 70% of the country's total hydrogen production. Industrial by-products such as chlor-alkali chemicals account for about 30% of hydrogen production.

2. The cost of hydrogen storage and transportation is too high. The hydrogen production sites in my country are far away from the central cities. Because the conditions for establishing long-distance hydrogen pipelines are not yet available, and the technology for mixing hydrogen in natural gas pipelines is not yet mature, the current domestic hydrogen transportation uses high-pressure trailers. Mainly, the weight of hydrogen carried by gas-hydrogen trailers only accounts for 1% to 2% of the total transportation weight, and the cost of storage and transportation per hundred kilometers is as high as 20 yuan/kg hydrogen.

3. The overall cost of hydrogen energy is too high. According to the current mainstream hydrogen production process in China, the cost of hydrogen production, storage and transportation and hydrogenation is considered comprehensively. The hydrogenation price for end users reaches 50-60 yuan/kg. Even if the renewable energy is considered to be 0.1 yuan/kwh, the cost is Will not reduce more. If a passenger car consumes 1kg of hydrogen per hundred kilometers and a diesel vehicle consumes 3kg of hydrogen per hundred kilometers, the cost of hydrogen has no advantage compared with fuel, and it is much more expensive than power battery cars.

Therefore, it is of great significance for promoting the application of hydrogen energy in cities to explore a method that can not only reduce carbon emissions throughout the life cycle, but also has good economy.

## 1.2 Potential advantages of hydrogen production in sewage treatment plants

Urban sewage contains a lot of energy, most of which exists in the form of biodegradable organic matter. At present, urban management departments consume energy to remove them and generate new carbon emissions. According to the statistics of the US EPA in 2006, the energy consumption of sewage treatment accounts for about 3% of the energy consumption of the United States, and nearly 50% of the electricity consumption is used for biological aeration. The energy contained in urban sewage is about 7-9 times the energy consumed for its treatment. In recent years, scientists have been committed to transforming urban sewage treatment plants into energy plants and resource plants and have achieved many results. Obtaining hydrogen energy from sewage is one of the potential directions of sewage energy. According to the basic principles of biofuel cells (MFCs), it is calculated theoretically that 1gCOD can convert 0.125g hydrogen, which shows that there are abundant hydrogen energy resources to be developed in urban sewage.

The basic principle of hydrogen production in sewage treatment is to disconnect the C chain or NH bond of pollutants in the sewage by electrochemical or biochemical methods. While obtaining gaseous  $H_2$ ,  $N_2$  and  $CH_4$ , it also reduces the content of organic matter and ammonia nitrogen in the water. This method couples the hydrogen production process with the sewage treatment process, and greatly reduces the sludge production of the sewage treatment plant. According to the understanding of the current technological progress, compared with the electricity consumption of water electrolysis for hydrogen production ( $>60\text{kWh/kgH}_2$ ), the electricity consumption of sewage treatment for hydrogen production will be significantly reduced, and the reduction in sewage treatment and sludge disposal costs can be partially compensated for the energy cost of the hydrogen production process further reduces the overall cost of hydrogen production.

Urban sewage treatment plants are generally distributed around cities, and the distances to the city center and various commercial and residential clusters are relatively close. They can take advantage of their unique location advantages

and establish independent hydrogen refueling stations, which can serve as heavy-duty trucks for inter-city transportation. It can also be integrated into the urban transportation system and serve the city's commercial vehicles such as urban logistics vehicles, garbage trucks, muck trucks, sprinklers, and buses. The hydrogen can also be compressed or liquefied, and then distributed to urban communities for use in community distributed fuel cell power generation or heating. Hydrogen production in the sewage treatment plant reduces the cost and risk of hydrogen long-distance transportation, conforms to the concept of distributed hydrogen production and utilization, can reduce the overall cost of hydrogen energy use, and promotes the use of urban clean energy and carbon emission reduction.

In summary, the development of the hydrogen production capacity of urban sewage plants and the use of renewable energy to obtain hydrogen energy while processing sewage will help promote the transformation of sewage treatment plants into energy factories and resource factories, and promote the application of hydrogen energy in cities, which greatly reduces the carbon emissions of the whole society, has obvious cost advantages and certain economic benefits, and is a topic worthy of in-depth study.

## **2. Introduction to common hydrogen production processes**

Organic matter (COD, BOD) in traditional wastewater is a kind of green energy. Some people have calculated the potential energy reserves in domestic sewage. The energy potential in sewage is 9~10 times higher than the energy consumed by sewage itself. In the process of sewage treatment, adding hydrogen production process can achieve the effect of water quality improvement and energy utilization. In the past few decades, the most mature development is hydrogen production from fossil fuels, which consumes a large number of non-renewable energy and emits greenhouse gas. Considering the current development status of China, the development of renewable energy hydrogen production process is the future trend. According to the technical category, mainly divided into pyrolysis gasification hydrogen, electrolytic water hydrogen, plasma hydrogen, semiconductor photocatalytic hydrogen, etc. The main way of large-scale industrial hydrogen production is pyrolysis and gasification. It is necessary to develop coupling hydrogen production in sewage plants, or use the “water” in sewage plants, or use the “pollution” in sewage. The common process for hydrogen production using “water” is electrolytic water. It is a new way to produce hydrogen by using “pollution” of wastewater treatment plant. There is a lack of relevant information. This section only introduces plasma hydrogen production.。

### **2.1 Pyrolysis gasification hydrogen production**

There are two main routes for producing hydrogen by cracking light hydrocarbons, propane dehydrogenation (PDH) and ethane cracking. Beginning in 2017, Chinese companies have started their efforts in the ethane-to-ethylene market, and many companies have successively announced that they will introduce low-cost light hydrocarbon feedstocks from the United States to produce ethylene. Propane dehydrogenation capacity is mainly concentrated in the eastern coastal areas of my country. The light hydrocarbon cracking hydrogen produces high purity, the lowest impurity content, and the purification difficulty is also small. However, due to raw materials, the cost is relatively high. According

to incomplete statistics, by the end of 2022, domestic ethylene production capacity will reach 8.58 million tons and by-product hydrogen 553,400 tons (1 ton of ethylene by-product 64.5kg hydrogen), theoretically capable of supplying 2.2 million fuel cell vehicles. The process flow is shown in Figure 2.1.

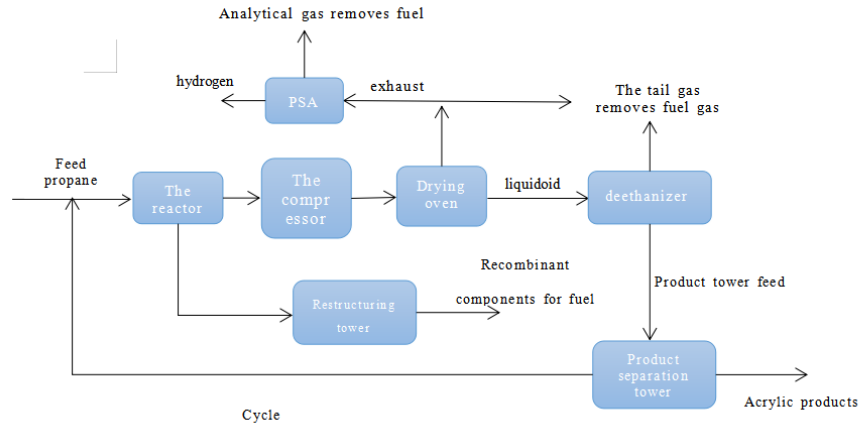


Figure 2.1 Process flow of light hydrocarbon cracking hydrogen production

## 2.2 Hydrogen production by electrolysis of water

As shown in Figure 2, hydrogen production from electrolyzed water is divided into acidic and alkaline components according to the electrolyte, and the principles are different.

(1) In alkaline and neutral media: the anode reaction is:  $2\text{OH}^- - 2\text{e}^- = \text{H}_2\text{O} + 1/2\text{O}_2\uparrow$

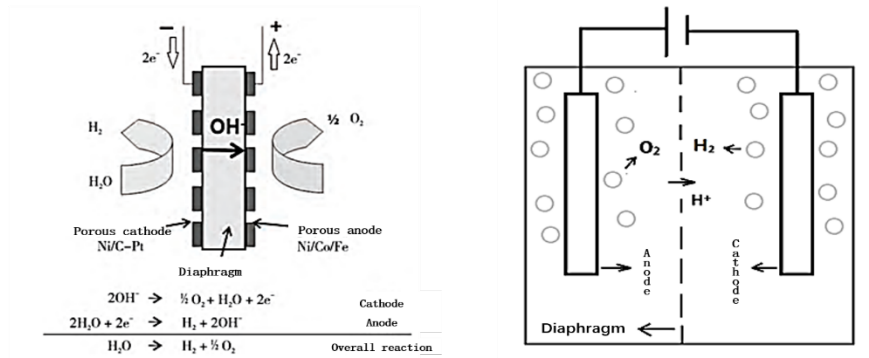
the cathode reaction is:  $2\text{H}_2\text{O} + 2\text{e}^- = 2\text{OH}^- + \text{H}_2\uparrow$

the total response is:  $2\text{H}_2\text{O} = 2\text{H}_2\uparrow + \text{O}_2\uparrow$

(2) In acidic medium: the anode reaction is:  $2\text{H}_2\text{O} - 4\text{e}^- = 4\text{H}^+ + \text{O}_2\uparrow$

the cathode reaction is:  $4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\uparrow$

the total response is:  $2\text{H}_2\text{O} = 2\text{H}_2\uparrow + \text{O}_2\uparrow$



**Figure 2.2 Schematic diagram of electrolyzed water under acidic (left) and alkaline (right) conditions**

Hydrogen production by electrolysis of water can be divided into three main categories: alkaline water electrolysis (ALK), proton exchange membrane (PEM) electrolysis of water, and solid oxide (SOEC) electrolysis of water.

Hydrogen production by alkaline electrolysis of water uses 30% potassium hydroxide solution or 25% sodium hydroxide solution as the electrolyte, and the working temperature is usually maintained at 70-90°C. Alkaline water hydrogen production electrolyzer is the core equipment of alkaline water electrolysis hydrogen production technology. The electrolytic cell is assembled by end pressure plates, gaskets, electrode plates, electrodes, permeable diaphragms and other parts.

The DC power supply supplies power to the alkaline water electrolyzer, and the electrolyte in the electrolyzer is decomposed to generate hydrogen and oxygen. The electrolyte containing oxygen enters the oxygen side separation and cooling device, the oxygen and the electrolyte are separated, and the electrolyte is returned to the alkaline water electrolysis tank. After the purity of the oxygen is tested, it is emptied or collected; the electrolyte containing hydrogen enters the hydrogen side for separation and cooling in the device, the hydrogen and the electrolyte are separated, and the electrolyte is returned to the alkaline water electrolyzer. After the purity of the hydrogen is tested, it is post-processed or collected.

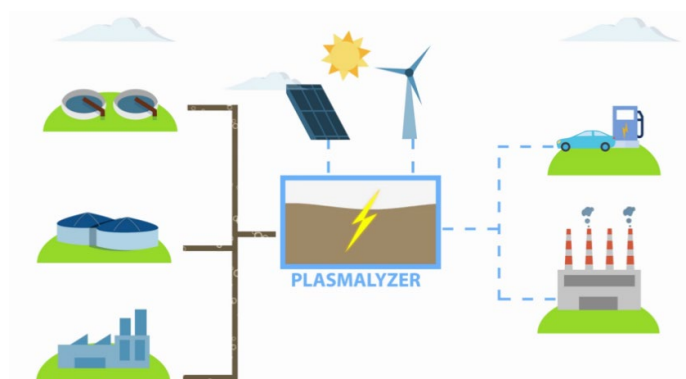
## 2.3 Plasma hydrogen production

Liquid-phase plasma hydrogen production technology is a new hydrogen



production technology. Since the liquid discharge used in the hydrogen production method generates plasma with high mass transfer efficiency, the hydrogen production effect is good, the hydrogen production is large, and the energy consumption of hydrogen production is low. Plasma hydrogen production method can produce hydrogen from various hydrogen-containing raw materials with a wide range of raw materials, which can avoid excessive dependence on non-renewable energy such as fossil fuels, and choose renewable energy such as ethanol and water. When other hydrocarbons are used as raw materials for hydrogen production, the plasma method can improve the flexibility and variability of the system, especially in vehicle hydrogen production.

Using plasma decomposition to produce hydrogen from the ionization of high-energy compounds in industrial wastewater, this technology not only converts pollutants in wastewater into valuable energy, but also reduces GHG emissions (carbon dioxide, carbon monoxide, hydrocarbons) by 30% to 60%, nitrogen oxide emissions can also be reduced by up to 60%. The use of high-energy compounds in wastewater to produce hydrogen can cut fuel production costs by half and significantly increase production. Plasma decomposition can create the sustainable “water-hydrogen-water cycle” required by the energy industry to achieve sustainable development, and represents an important key link for the successful introduction of storage and fuel cell technology.



**Figure 2.3 Schematic diagram of plasma production of hydrogen**

### **3. Research content and framework**

#### **3.1 The goal and purpose of research**

Based on the above background, the research objectives of this report are as follows:

The project plans to conduct systematic research on the technological development direction and R&D application stage of hydrogen production from sewage at home and abroad, and use a sewage treatment plant in Hunan as a research case to construct a life cycle list of sewage hydrogen production processes.

Taking the electrolysis of alkaline water as the research object, a complete life cycle assessment model is established to quantitatively evaluate the impact of the process on the environment during the construction and operation phases.

According to the results of the life cycle assessment, identify the key processes in the life cycle of the electrolytic alkaline water hydrogen production process, seek feasible methods to reduce environmental impact, and identify the key processes that generate costs in the process, and put forward effective suggestions for reducing costs, from environmental and economic perspectives. Two aspects of cost provide a scientific basis for optimizing the process of hydrogen production from sewage.

This study uses life cycle assessment methods and life cycle cost analysis to evaluate the carbon emissions and benefit analysis of the electrolytic alkaline water hydrogen production process during the life cycle. Through the above research, it is revealed that the use of renewable energy to combine sewage treatment with hydrogen production The economic and ecological value of the coupling process of the company is analyzed, and the policy bottlenecks that may be encountered in the development and promotion process are analyzed, and relevant suggestions are made.

#### **3.2 Research content and technical route**

Based on the background research of sewage treatment and traditional hydrogen production process, the electrolysis alkaline water hydrogen production is selected as the research object, and the carbon emissions and economic benefits

of the process during the life cycle are analyzed. The specific content is as follows:

### **3.2.1 Determine research objectives and scope**

Through the investigation of the Hunan Sewage Treatment Plant and the process of hydrogen production by electrolysis of water at home and abroad, refer to relevant documents to determine the research objectives and system boundaries.

### **3.2.2 Life cycle inventory analysis**

Through on-site inspections and reference to relevant documents, the inventory data of the hydrogen production process from electrolysis of water in the life cycle is determined. Secondly, determine the list price of materials and energy consumption for the process by inquiring on the Internet and contacting raw material suppliers.

### **3.2.3 Life cycle impact assessment**

According to the life cycle inventory, modeling in the simpro software, the IPCC 2013 method is selected for analysis, and the carbon emissions during the life cycle of the electrolysis of alkaline water for hydrogen production are calculated. According to the analysis results, identify the main factors of the environmental impact of the process during the life cycle.

### **3.2.4 Life cycle cost analysis**

The value of the environment and natural resources needs to be assessed in the decision-making process of environmental protection and economic operation. Life cycle cost analysis is used to measure and monetize the value of environment and natural resources. The results of life cycle cost analysis provide information support for the decision-making of the process in the life cycle.

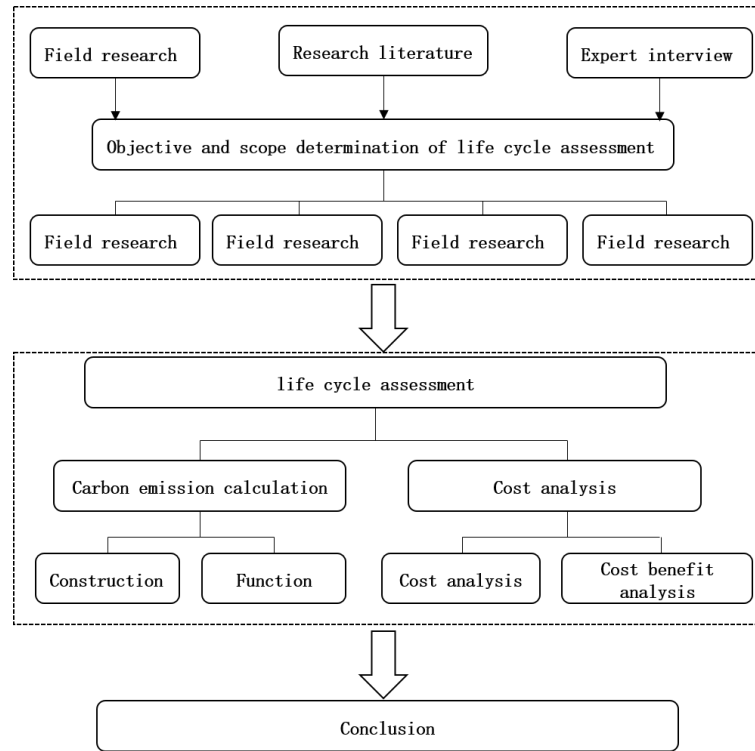


Figure 2.4 Technical route

### 3.3 Research of Carbon Emission Based on LCA Method

LCA is the compilation and evaluation of input, output and potential environmental impacts in the life cycle of a product or system. This LCA method is usually implemented by following the ISO 14040:2006 and 14044:2006 standards. LCA is considered to be the most powerful tool for assessing the environmental impact of any product, unit process or process system. Life cycle assessment (LCA) is a kind of environmental management technology, which takes into account the direct and indirect environmental load and environmental benefits generated by the stages and links of the whole life cycle of the evaluation object. LCA mainly focuses on the environmental impact of the evaluation object, and usually does not involve the social and economic factors of the evaluation object. However, life cycle assessment research can be combined with social and economic factors. For example, LCA can be combination with life cycle cost (LCC) and social life cycle assessment (SLCA).

#### 3.3.1 System boundary

Determine the system boundary, that is, determine the unit process to be

included in the system. We cannot trace all inputs and outputs of a process system and must define the boundaries of the system. By excluding some parts, i.e., ignoring them in the system, the results may be distorted. However, it is not necessary to quantify the input and output that have little impact on the overall research conclusions.

The system boundary of this study carries out the life cycle assessment of hydrogen production from electrolytic water from the construction stage and operation stage. In the construction stage, the production and transportation of raw materials for photovoltaic panels and alkaline water electrolysis are mainly considered, and the traditional sewage treatment process is not considered. The reason is that the hydrogen production from electrolytic water does not have a great impact on the original process. The output of hydrogen production from alkaline water electrolysis in the operation stage is mainly hydrogen produced by electrolysis. Specific system boundaries are shown in Figure 2.5.

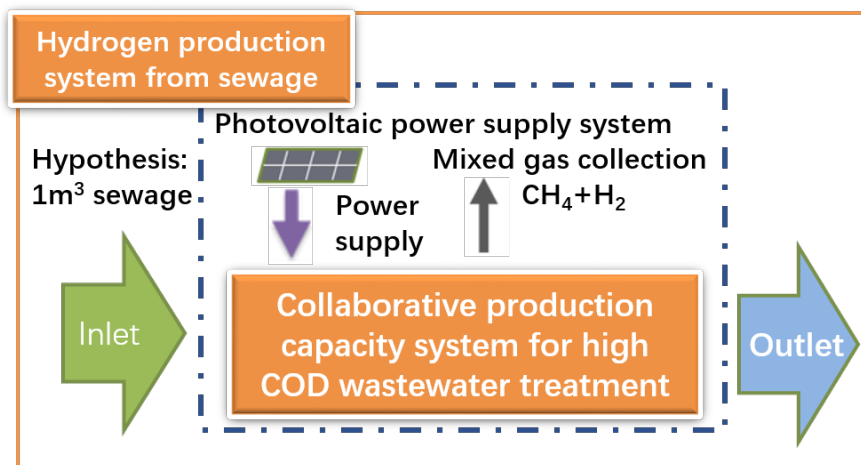


Figure 2.5 System boundary

### 3.3.2 Functional unit

One of the main purposes of functional units is to normalize the input and output data and provide benchmarks from a mathematical perspective. Therefore, functional units should be clearly defined and measured. In order to quantify the carbon emission during the whole life cycle of electrolysis alkaline water for hydrogen production, the functional unit is defined as the electrolysis water for hydrogen production system required to treat 1 m<sup>3</sup> wastewater every day in the

25-year life cycle.

### 3.3.3 Evaluation methods and software

Based on the definition of research objectives, this study chose to analyze the Global Warming Potential (GWP) of the life cycle of electrolysis alkaline water for hydrogen production, because GWP is an environmental impact indicator used to quantify carbon emissions from products or processes.

The selection of quantitative evaluation method of carbon footprint meets the requirements of ISO14067: 2013, PAS2050: 2011, ISO14040: 2006, ISO14044: 2006, and considers the scientificity of the method, the availability of characteristic factors and the applicability of the method. Table 2.1 shows the environmental impact and evaluation model.

**Table 2.1 Types of environmental impacts and evaluation models**

Environmental impact type	Evaluation model	Contribution material	Influence type parameter	Method source	Impact type characteristics
(Global Warming Potential, GWP)	Berne Model-Global Warming Potential for 100 Years	CO <sub>2</sub> 、CH <sub>4</sub> 、CFCetc.	kg CO <sub>2</sub> eq.	IPCC, 2013	Types of global influence

Global Warming Potential (GWP): The method proposed by the IPCC Fifth Assessment Report (2013) to calculate the GWP value of the product life cycle. The IPCC (2013) method covers a variety of characteristic substances, including carbon dioxide (CO<sub>2</sub>), Methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), carbon tetrafluoride (CF<sub>4</sub>), hexafluoroethane (C<sub>2</sub>F<sub>6</sub>), sulfur hexafluoride (SF<sub>6</sub>), hydrofluorocarbon (HFC) and halon, etc. This method is based on the relative radiative influence value of other greenhouse gases compared with carbon dioxide in a 100-year time frame, that is, the characterization factor, which is used to convert the emissions of other greenhouse gases into CO<sub>2</sub> equivalent (CO<sub>2</sub> eq.). For example, the impact of 1kg of methane on global warming in 100 years is equivalent to the impact of 28kg of carbon dioxide emissions on global warming, so based on the carbon dioxide equivalent (CO<sub>2</sub> eq.), the characteristic factor for methane is 28 kgCO<sub>2</sub>

eq.

In the research, Simapro9 software was used to build the life cycle model of the process and calculate the carbon footprint results. Simapro is a professional LCA software developed by Pre Consultant, Dutch, which supports full life cycle process analysis. It has built-in Swiss Ecoinvent database, European Life Cycle Reference Database (ELCD), Agri-footprint, USLCI and other databases. In this study, data sets in the Ecoinvent, ELCD, USLCI, and Agri-footprint databases were used.

Ecoinvent database is developed by Swiss Life Cycle Research Center, including data from Western Europe, Switzerland, China and other regions. The database contains more than 10000 product and service data sets, involving chemical, energy, transportation, building materials, electronics, pulp and paper, waste treatment and agriculture.

### **3.3.4 Related assumptions**

In the process of product or system life cycle assessment, in order to reduce the workload in the calculation process, reasonable assumptions can be made within the scope of the study, assumptions should be made clear explanation.

It is assumed that the process of hydrogen production from electrolytic alkaline water does not affect the original sewage treatment process, so the research content does not include the research on sewage treatment process.

At present, due to the lack of project research on hydrogen production from electrolytic wastewater and the lack of relevant references, this report chooses electrolytic alkaline water as the research object.

### **3.3.5 Data selection principle**

Based on the investigation and analysis of LCA research on various product processes at home and abroad, and referring to the requirements of trade-off criteria in the Product Environment Footprint (PEF) guidelines issued by the European Union in 2013, the basic trade-off principles areas follows:

1. Proportion based on inputs: the material energy input with the quality or energy input less than 2 % is discarded, but the total proportion of the product input is not more than 5 %. However, for substances with small quality but large

life cycle environmental impact, they cannot be abandoned, such as gold and silver;

2. Proportion based on environmental impact: similar inputs are used to exclude raw materials with less actual impact. For any class of effects, if the same effect is less than 1 % in the sum of a process / activity, the process can be discarded from the system boundary;

3. Ignore the means of production and infrastructure.

### 3.4 Life cycle cost analysis

#### 3.4.1 Project cost analysis

##### Initial investment cost analysis

The sewage treatment plant of this project will build a photovoltaic system to obtain renewable energy hydrogen through the process of electrolyzing alkaline water to produce hydrogen. The project will set up a photovoltaic system, a sewage disposal co-production system and a mixed gas collection system.

The photovoltaic system of this project will be mainly set up above the pool and green land (not less than 6 meters). The photovoltaic module is installed in the form of steel structure and prestressed steel cable support, so the span is large. Compared with the traditional ground photovoltaic power station, it can fully improve the spatial utilization rate. Installation of photovoltaic modules specification, neat arrangement, good lighting permeability, does not affect the growth of vegetation. Avoid direct sunlight, reduce the growth of green algae, and reduce the cost of manual cleaning and mechanical washing.

The initial investment cost  $S_i$ , includes:

(1) Equipment purchase fee  $S_e$

(2) Software and hardware purchase fees  $S_{in}$

(3) Construction engineering fee  $S_c$

(4) 25-year land cost  $S_l$

(5) Other costs (project management fees, survey and design fees, technical service fees)  $S_o$

$$S_i = S_e + S_{in} + S_c + S_l + S_o$$

Initial cost total investment = total power  $\times$  system cost per watt



### Operational cost analysis

Operating costs include management costs, routine maintenance costs (refers to the total cost of daily maintenance of all buildings and equipment of photovoltaic panels), accidental maintenance costs. Due to the long life of photovoltaic panel equipment ( $\geq 25$  years), the impact of inflation rate and social discount rate on the total cost should be considered when establishing the operation cost evaluation model. Assuming a (%) inflation rate,  $r$  (%) social discount rate and  $n$  (year) lifetime of photovoltaic systems.

Operating cost = total power  $\times$  system maintenance cost per watt

In the  $i$  year ( $i \leq 25$ ), the operating cost is

$$S_i = \frac{\text{Labor cost} + \text{Management fee (year)}}{(1 + r - a)^{i-1}}$$

### 3.4.2 Project income assessment

The energy input in the operation stage is all from the photovoltaic system, so the energy input is 0, and the hydrogen produced by electrolysis is sold.

Without considering the financial subsidies of the central and local governments, the calculation formula of the photovoltaic system power generation in the first year is as follows: the photovoltaic system power generation in the first year = the total power of the photovoltaic system  $\times$  the average peak sunshine hours  $\times 365$  days  $\times$  the energy efficiency factor of the photovoltaic system. Unit power generation within 25 years of life cycle can be calculated and total hydrogen production can be obtained.

Project revenue  $B_i$  = total amount of hydrogen produced  $\times$  selling price per ton of hydrogen

When the project income is greater than the total cost of the project input, the project can be considered to start to reap rewards.

$$\text{Return on investment ROI} = \frac{\text{Project income } B_i}{\text{Total project investment cost}} \times 100\%$$

### 3.4.3 Project cost-benefit analysis

#### Present value calculation

The present value of the benefits or costs obtained in the  $n$ th year in the future is determined by the following formula:

$$PV(B_n \text{ or } C_n) = \frac{B_n \text{ or } C_n}{(1 + r)^n}$$

In formula:

$PV(B_n)$  : present value of benefits;

$PV(C_n)$  : present value of cost;;

$B_n, C_n$  : Benefits and expenses incurred in the nth year;

$r$  : social discount rate;

$n$  : calculation period, year.

#### **Economic Net Present Value ENPV**

Economic net present value (ENPV) is an absolute indicator reflecting the net contribution of projects to the national economy. Items with economic net present value greater than zero or equal to zero can be considered.

$$ENPV = \sum_{i=0}^n \frac{TB_i - TC_i}{(1 + r)^n}$$

In formula:

$TB_i, TC_i$  : the total benefit and total cost incurred in the i-th year;

$r$  : social discount rate;

$n$  : calculation period, year.

## 4. Collection and Analysis of Life Cycle List of Hydrogen Production by Electrolysis of Alkaline Water

Listing analysis includes data collection and calculation to quantify input and output in the product system. Inventory analysis is based on the data of resources, energy consumption and pollutant emissions throughout the life cycle, and it is an objective quantitative process impact assessment of the evaluation object. In the implementation of LCA, the most difficult task is to collect data. Although there are large amounts of available data in the database, some data may not be applicable due to geographical problems. The inventory data of this report are mainly collected and analyzed from the construction stage and the operation stage. The data are from field research and literature reference.

### 4.1 Data processing

The collection of inventory data is based on the functional unit, that is, the electrolysis water hydrogen production system needed to treat 1 m<sup>3</sup> wastewater every day in the 25-year life cycle. According to the daily sewage treatment amount, the life of photovoltaic panels and electrolyzers is counted to obtain the data of the construction stage in the 25-year life cycle.

According to the industrialization data provided by Suzhou Jingli Institute, the electrolysis alkaline water hydrogen production system electrolyzes 1m<sup>3</sup> of pure water, assuming an energy conversion rate of 60%, and a power consumption of 6666.7 kWh. In the end, 111 kg of hydrogen can be produced. Treating 1m<sup>3</sup> of sewage per day, operating for 25 years, the total hydrogen production is 1013.9 tons of hydrogen, and the power consumption is 6.08×10<sup>7</sup> kWh.

The grid power generation  $E_p$  of the photovoltaic system is calculated as follows:

$$E_p = H \times P \times K_1$$

$P$ ——is install capacity for the system (kWp)

$H$ ——is the local standard hours of sunshine

$K_1$ ——is the overall efficiency of the system

The average annual sunshine time under standard illumination in Hunan area

is 3.1-3.8h. This report takes 3.29h. The overall efficiency of the system is a correction coefficient after considering various factors. The general value is 75%-85%. The overall efficiency is 80%. Then the system installation capacity P:

$$P=E_p\div H\div K_1$$

The calculated system installation capacity is 2532kWp

Since the normal service life of the photovoltaic system is 25 years, it does not need to be replaced during the life cycle. The service life of the electrolysis water hydrogen production equipment is 15 years, so the statistical inventory data during the life cycle is the materials and energy consumption required for the production of 1.67 groups of equipment.

## **4.2 List collection and analysis during the construction phase**

The collection of inventory data is based on the functional unit, that is, the electrolysis water hydrogen production system needed to treat 1 m<sup>3</sup> wastewater every day in the 25-year life cycle. According to the daily sewage treatment amount, the life of photovoltaic panels and electrolyzers is counted to obtain the data of the construction stage in the 25-year life cycle.

### **4.2.1 PV panel production stage data**

The production of photovoltaic systems mainly includes the production of cells and battery modules.

The cell production process mainly includes: texturing, cleaning before diffusion, phosphorus diffusion, PSG removal, edge etching, coating, screen printing, burning, testing and grading. The texturing process mainly uses nitric acid and hydrofluoric acid to corrode the silicon wafer, and then undergoes a pickling process to remove water, metal ions and other magazines on the surface of the silicon wafer. Then, a p-n junction is formed through a diffusion process, and hydrofluoric acid is used to remove the phosphorous silicate glass on the surface. Next, Si H<sub>4</sub> and NH<sub>3</sub> are used to generate plasma under the action of high-frequency glow discharge. The plasma is adsorbed on the surface of the silicon wafer and reacts to form a silicon nitride film on the surface of the silicon wafer. Finally, it is printed and burned to form a cell. The cell data comes from the Ecoinvent database.

The manufacturing of crystalline silicon solar cell modules mainly uses

materials such as tempered glass and EVA to monolithically interconnect and encapsulate crystalline silicon solar cells to protect electrode contact, prevent interconnection lines from corrosion, and avoid cell chipping. Packaging quality directly affects the service life of crystalline silicon solar cell modules. The list data of photovoltaic modules in production are shown in Table 2.2

**Table 2.2 List data of photovoltaic module production process**

name	material	data	mode of transport	transport distance
cell	cell	15923m <sup>2</sup>	truck	100Km
copper	copper	1.24 t	truck	20Km
fresh water	water	882680 t	truck	21Km
EVA film	EVA	17.88 t	truck	13Km
TPT backplane	Polyvinyl fluoride	9.22 t	truck	17Km
Tempered glass	glass	157.5 t	truck	15Km
Organic silica gel	Silica gel	101.28 t	truck	56Km
Aluminum frame	aluminum	33.22 t	truck	10Km
production energy consumption	electricity	148122 kWh	/	/

#### 4.2.2 Production stage data of electrolysis equipment

The material list of electrolysis equipment that processes 1m<sup>3</sup> sewage every day and has been in operation for 25 years is shown in Table 2.3. Alkaline water hydrogen production electrolyzers have various internal structures, which can be basically divided into oxygen electrolysis, hydrogen electrode, electrolyte, connection part and frame. The data source refers to the research and analysis of Guangling Zhao et al. on electrolyzed water technology. The hydrogen electrode, oxygen electrode and connecting parts in the traditional electrolysis tank are all made of the same material. Choosing a nickel plate with a higher density can meet the requirements of the above three components. The oxygen electrode is usually nickel, so a simple nickel plate or a nickel-plated steel plate with an open geometry is usually used. This report selects porous solid nickel plates. Hydrogen electrodes are usually made of different kinds of active nickel plates. In this study, we select nickel plates with nickel sulfide coating on the surface. Nickel plates

and diaphragms (porous separators between the electrodes, formerly asbestos) are then alternately stacked in a suitable frame to ensure that there is a large space between the water electrolyte and the gas. The membrane is reinforced by a polyphenylene sulfide (PPS) mesh, with a total porosity of approximately 50%. The diaphragm can be prepared by the reverse phase immersion precipitation method. The electrolyte is 30% potassium hydroxide solution, and the frame is made of stainless steel. Electricity is the main energy used in the equipment assembly process.

**Table 2.3 List of production process data of electrolysis equipment**

name	material	data	mode of transport	transport distance
oxygen electrode	nickel plate	39.2Kg	truck	85Km
hydrogen electrode	nickel plate	39.2Kg	truck	85Km
	nickel sulfide coating	1.4Kg	truck	30Km
electrolyte	30% potassium hydroxide	20.8Kg	truck	15Km
connection material	nickel plate	170.3Kg	truck	85Km
frame	polyphenylene sulfide	70.79Kg	truck	15Km
	stainless steel	84.8Kg	truck	10Km
production energy consumption	electricity	50.3kWh	/	/

### 4.3 List collection and analysis during operation phase

The energy input in the operation phase is all from the photovoltaic system, so the energy input is zero, and all the hydrogen produced by electrolysis is sold. Assuming that all hydrogen is burned to generate electricity, under normal temperature and pressure conditions, the combustion value of hydrogen is  $1.43 \times 10^8 \text{ J/kg}$ , and the heat released by the combustion of 1kg of hydrogen is equivalent to 39.7 kWh of electricity. 1013.9t of hydrogen can indirectly reduce the production of  $4.0 \times 10^7 \text{ kWh}$  of electricity.

## 5. Calculation of Carbon Emissions in the Life Cycle of Electrolyzed Water Hydrogen Production

### 5.1 Carbon emissions during the construction phase

The carbon dioxide emissions during the construction phase are  $4.34 \times 10^6$  kg CO<sub>2</sub> eq. The carbon dioxide emissions of photovoltaic modules accounted for 99.9% of the entire construction phase.

#### 5.1.1 Carbon emissions during the production phase of photovoltaic modules

The carbon emission during the photovoltaic module production stage is  $4.34 \times 10^6$  kg CO<sub>2</sub> eq. The CO<sub>2</sub> emissions from the production of polycrystalline silicon cells are  $2.76 \times 10^6$  kg CO<sub>2</sub> eq, accounting for 63.6% of the production stage, and are the main source of CO<sub>2</sub> emissions. The production process of photovoltaic modules consumes a lot of water resources. The carbon emission during the production of clean water is  $4.97 \times 10^5$  kg CO<sub>2</sub> eq, which accounts for 15.5% of this stage. Followed by the production of silica gel and tempered glass, accounting for 7.75% and 6.67% respectively. The carbon emissions during the production phase of photovoltaic modules are shown in Figure 2.6.

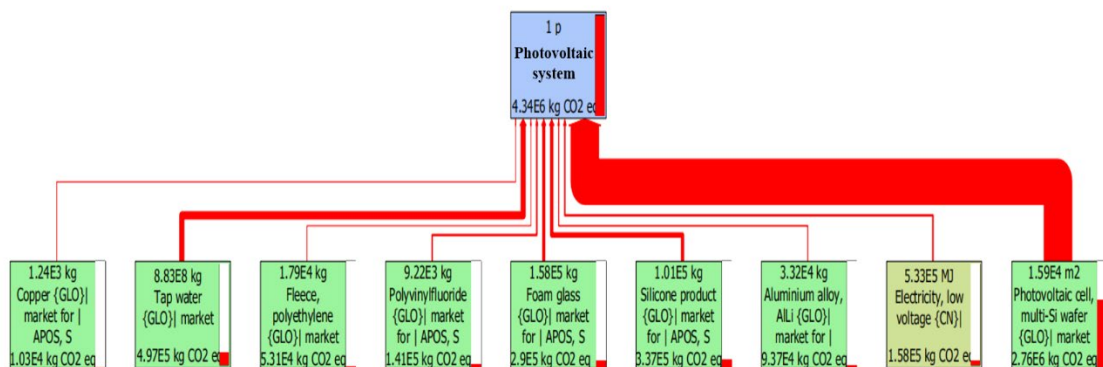


Figure 2.6 Carbon emissions during the production phase of photovoltaic modules

### 5.1.2 Carbon emissions during the production phase of electrolysis equipment

The carbon emission during the production stage of the electrolysis equipment is  $3.47 \times 10^3$  kg CO<sub>2</sub> eq. The most used material in the production process of electrolyzers is nickel plate, which is also the main source of carbon emissions in the production process. The connection material used 170 kg of nickel plates, which produced  $1.86 \times 10^3$  kg CO<sub>2</sub> eq, which accounted for 53.5% of the carbon emissions at this stage. The carbon emissions of polyphenylene sulfide and stainless steel accounted for 14.4% and 5.73%, respectively. Carbon emissions from nickel sulfide and energy consumption during assembly are negligible. Figure 2.7 shows the results of carbon emissions during the production stage of electrolysis equipment.

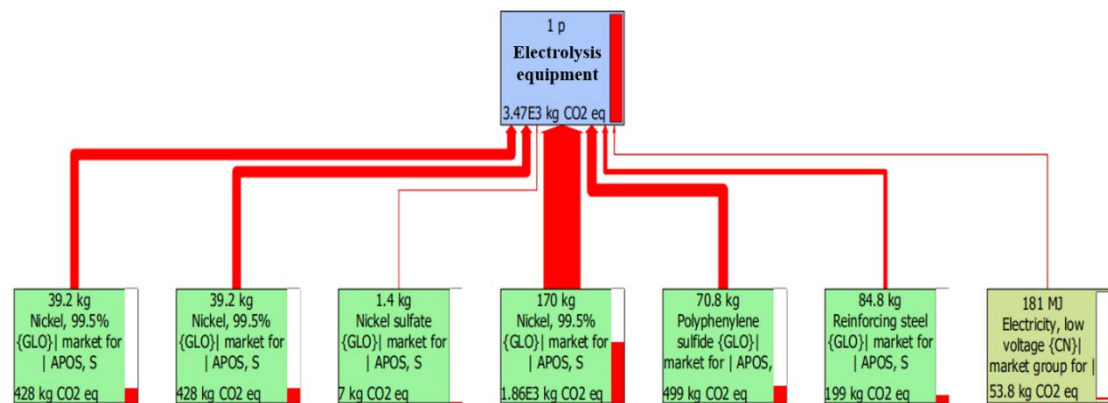


Figure 2.7 Carbon emissions during the production stage of electrolysis equipment

### 5.2 Carbon emissions during operation

Carbon emissions during the operation phase  $-4.28 \times 10^7$  kg CO<sub>2</sub> eq. The hydrogen produced can indirectly reduce the production of electricity from the national grid, thereby reducing carbon dioxide emissions.



### 5.3 Overall life cycle assessment of construction and operation

The carbon emissions of hydrogen production from electrolysis of water during the 25-year life cycle are  $-3.84 \times 10^7$  kg CO<sub>2</sub> eq. The environmental benefit generated during the operation phase is about 10 times that of the construction phase.

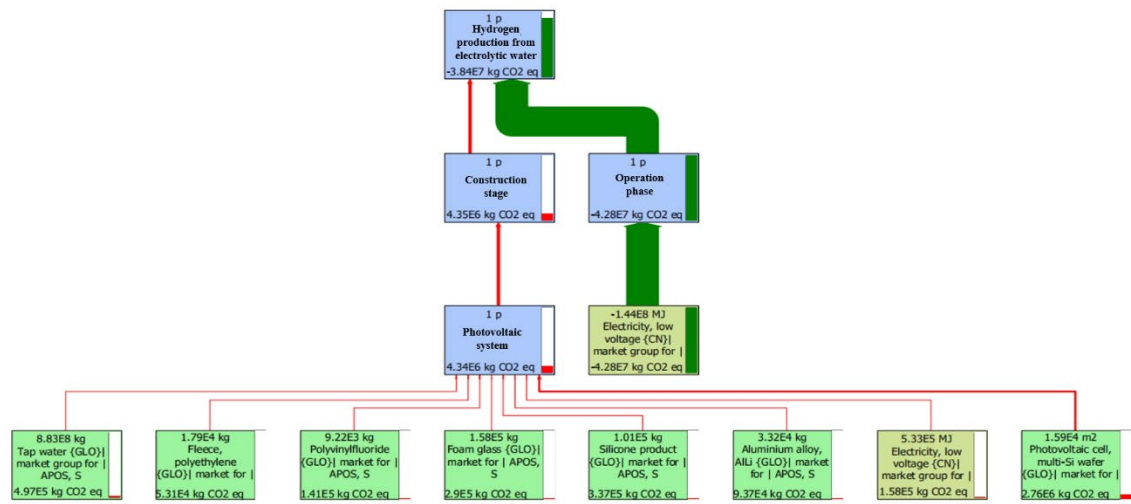


Figure 2.8 25-year life cycle of hydrogen production from electrolysis of water

## **6. Collection and analysis of life cycle economic inventory**

### **6.1 Project cost**

#### **6.1.1 Initial investment cost**

##### **1. Photovoltaic system**

According to our survey results, in 2020, the cost of ordinary ground photovoltaic power plants has been greatly reduced, about 3.35 yuan/Wp; such as this project's high-altitude suspension cable structure, its cost is only 4-4.5 yuan/Wp, This project costs 4 yuan/Wp.

The installed capacity of the photovoltaic system of this project is 2743kWp, then:

Initial investment cost of the project

= PV system installed capacity × unit cost

= 2743 kWp×4 yuan/Wp×1000 = 10.97 million yuan

among them:

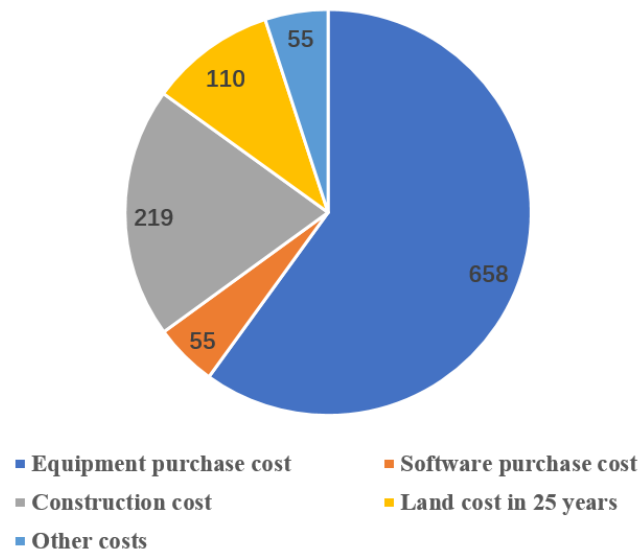
(1) Equipment purchase cost  $S_e$  accounts for about 60% of the total investment, which is about 6.58 million yuan.

(2) Software and hardware purchase cost  $S_{in}$  accounts for about 5% of the total investment, about 550,000 yuan.

(3) The construction cost  $S_c$  accounts for about 20% of the total investment, which is about 2.19 million yuan.

(4) 25-year land cost  $S_l$  accounts for about 10% of the total investment, about 1.1 million yuan.

(5) Other costs (project management fees, survey and design fees, technical service fees)  $S_o$  accounted for about 5% of the total investment, about 550,000 yuan.



**Figure 2.9 The composition and details of initial investment costs (ten thousand yuan)**

## 2. Hydrogen production system

This project selects an alkaline water electrolysis hydrogen production equipment with a rated hydrogen output of 1000m<sup>3</sup>/h. The cost of the equipment to synthesize a unit cubic meter of hydrogen is 13 yuan/kg. This project treats 1m<sup>3</sup> of sewage every day. After 25 years of operation, the total hydrogen production is 1013.9 tons of hydrogen, which is about 1013900 kg of hydrogen.

Initial investment cost of the project

= Total hydrogen production × unit cost

= 1013900kg × 13 yuan/kg = 13.18 million yuan

Therefore, the initial total investment cost of this project is: 10.97 million yuan + 13.18 million yuan = 24.15 million yuan.

## 6.1.2 Operating cost

### 1. Photovoltaic system

According to the survey, in 2020, it is reasonable to take 4 cents/Wp per year for the maintenance fee of the photovoltaic system. Therefore, the operating costs for the first year are:

$S_1 = \text{total power} \times \text{system maintenance cost per watt}$

= 2743 kWp × 4 minutes/Wp × 1000 = 110,000 yuan/year

## 2. Electrolysis hydrogen production system

The maintenance cost of hydrogen production by alkaline electrolysis is about 3.15 yuan/kg per year, and the annual hydrogen production is 40556kg. Therefore, the operating cost for the first year is:

$$\begin{aligned} S_1 &= \text{Annual hydrogen production} \times \text{system maintenance cost per kg} \\ &= 40556\text{kg} \times 3.15 \text{ yuan/kg} = 128,000 \text{ yuan/year} \end{aligned}$$

Due to the long life of photovoltaic panels and hydrogen production equipment ( $\geq 25$  years), the impact of inflation rate and social discount rate on the total cost should be considered when establishing an operating cost evaluation model. According to the "Construction Project Economic Evaluation Methods and Parameters (3rd Edition)" issued by the National Development and Reform Commission, the social discount rate  $r$  is 8%, the inflation rate  $a$  is 4%, and the life of photovoltaic panel equipment is 25.

In the  $i$  year ( $i \leq 25$ ), the operating cost is

$$S_i = \frac{\text{Labor fee} + \text{management fee (year)}}{(1 + r - a)^{i-1}}$$

### 6.1.3 Project life cycle cost estimation

The 25-year life cycle cost of this project is estimated as follows:

**Table 2.4 25-year life cycle cost schedule of the project**

Years	Initial investment cost of the project (ten thousand yuan)	Operating expenses (ten thousand yuan)	Total cost (ten thousand yuan)
0	2,415.00	-	2,415.00
1	-	23.80	23.80
2	-	22.88	22.88
3	-	22.00	22.00
4	-	21.16	21.16
5	-	20.34	20.34
6	-	19.56	19.56
7	-	18.81	18.81
8	-	18.09	18.09

9	-	17.39	17.39
10	-	16.72	16.72
11	-	16.08	16.08
12	-	15.46	15.46
13	-	14.87	14.87
14	-	14.29	14.29
15	-	13.74	13.74
16	-	13.22	13.22
17	-	12.71	12.71
18	-	12.22	12.22
19	-	11.75	11.75
20	-	11.30	11.30
21	-	10.86	10.86
22	-	10.44	10.44
23	-	10.04	10.04
24	-	9.66	9.66
25	-	9.28	9.28
总和	<b>2,415.00</b>	<b>386.68</b>	<b>2,801.68</b>

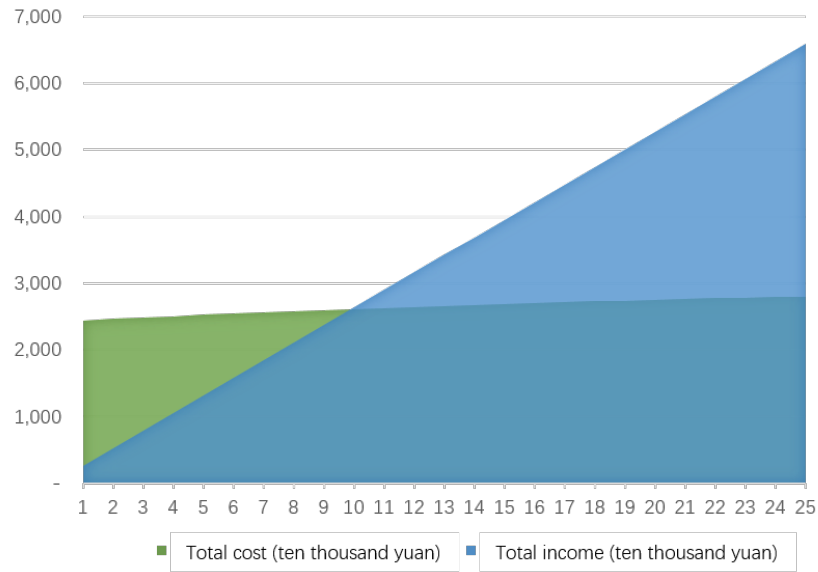
As shown in the table, the total 25-year life cycle cost of the photovoltaic system of this project is approximately 28.02 million yuan.

## 6.2 Project income

The energy input in the operation phase is all from the photovoltaic system, so the energy input is zero, and all the hydrogen produced by electrolysis is sold. The total hydrogen production of this project in 25 years is 1013.9 tons. Currently, the unsubsidized price of hydrogen in the market averages 65 yuan per kilogram.

Project revenue  $B_i$  = total hydrogen production  $\times$  hydrogen price per ton = 1013900 kg $\times$ 65 yuan/kg =65.9 million yuan. When the project income is greater than the total cost of the project input, the project can be considered to start to

reap rewards.



**Figure 2.10 Annual cumulative total cost and total revenue of the project (ten thousand yuan)**

As shown in Figure 2.10, in the 10th year, the project is expected to accumulate total income of 26.36 million yuan. In the same year, the cumulative total cost of the project is approximately 26.16 million yuan. It can be considered that the project began to receive returns in that year.

$$\text{Return on investment ROI} = \frac{\text{Project income Bi}}{\text{Total project investment cost}} \times 100\%$$

$$= \frac{6590}{2802} \times 100\% = 2.35\%$$

The rate of return on investment of this project is 2.35%.

### 6.3 Cost-benefit evaluation

According to the calculation formula of economic net present value (ENPV), the annual ENPV value can be calculated, as shown in the following table.

**Table 2.5 Annual ENPV calculation results**

Years	Total cost (ten thousand yuan)	Total income (ten thousand yuan)	TB-TC (ten thousand yuan)	ENPV
0	2,415.00	-	-2,415.00	-2,415.00
1	23.80	263.60	239.80	222.04

2	22.88	263.60	240.72	206.37
3	22.00	263.60	241.60	191.79
4	21.16	263.60	242.44	178.20
5	20.34	263.60	243.26	165.56
6	19.56	263.60	244.04	153.79
7	18.81	263.60	244.79	142.83
8	18.09	263.60	245.51	132.64
9	17.39	263.60	246.21	123.17
10	16.72	263.60	246.88	114.35
11	16.08	263.60	247.52	106.16
12	15.46	263.60	248.14	98.54
13	14.87	263.60	248.73	91.46
14	14.29	263.60	249.31	84.88
15	13.74	263.60	249.86	78.77
16	13.22	263.60	250.38	73.08
17	12.71	263.60	250.89	67.81
18	12.22	263.60	251.38	62.91
19	11.75	263.60	251.85	58.36
20	11.30	263.60	252.30	54.13
21	10.86	263.60	252.74	50.21
22	10.44	263.60	253.16	46.57
23	10.04	263.60	253.56	43.18
24	9.66	263.60	253.94	40.05
25	9.28	263.60	254.32	37.13
总计	2,801.68	6,590.00	3,788.32	<b>208.97</b>

The economic net present value of this project is 209, and the net present value is greater than zero. Therefore, it is considered that the project has a large

net contribution to the national economy during its life cycle and is a project that can be considered.

## **7. Conclusion**

This paper aims to study the carbon emissions and cost analysis of the



electrolysis alkaline water hydrogen production system during the 25-year life cycle. Through the inventory analysis, SimaPro9 software and the IPCC 2013 impact assessment method are used to simulate the electrolysis alkaline water hydrogen production system. Through case analysis and research, the life cycle assessment of the 25-year life cycle of the electrolysis alkaline water hydrogen production system is carried out in two aspects: the construction phase and the operation phase. The conclusions are as follows:

1. In terms of overall environmental impact, the carbon emissions of hydrogen production from electrolysis of water during the 25-year life cycle are  $-3.84 \times 10^7$  kg CO<sub>2</sub> eq. The operation stage has the greatest impact on the environment, indirectly reducing the emissions of  $4.28 \times 10^7$  kg CO<sub>2</sub> eq.

2. The hydrogen production system by electrolysis of alkaline water will only produce carbon emissions during the construction phase. The source of carbon emissions is mainly the production of polysilicon batteries, which account for 63% of the carbon emissions during the construction phase. In order to improve the environmental benefits of the system, the production process of polycrystalline silicon cells can be improved to reduce carbon emissions during the production process.

3. The estimated total investment of this project is 28.02 million yuan, including initial system construction and equipment investment costs totaling 24.15 million yuan and 25-year operating costs totaling 3.87 million yuan. The total hydrogen production of the project in 25 years is 1013.9 tons. The hydrogen will be sold directly. The total income of the project in 25 years is 65.9 million yuan. Through calculation and analysis, this project will achieve a return in the tenth year, with a return on investment of 2.35%. In order to evaluate the environmental and economic benefits of the project, the economic net present value is used for evaluation. The economic net present value of the project is 209, which is greater than zero. Therefore, it is considered that the project has a large net contribution to the national economy during its life cycle and is an investment project that can be considered.

## **Chapter III Analysis of Policy Obstacles to Hydrogen Production in Wastewater Treatment Plants**

### **Abstract**

This project intends to make full use of the distributed and high floor area ratio of the urban sewage treatment plant to build a solar photovoltaic power station in the plant. On the one hand, the generated electricity is supplied to the sewage treatment plant for daily use, and on the other hand, the excess electricity will be used for the electrolysis of water in the sewage plant to produce hydrogen, and the produced hydrogen will be supplied to the hydrogen refueling station or used as a hydrogen fuel cell.

The report first analyzes the problems of policies, regulations, management mechanisms, and standard systems that exist in the sewage treatment plant construction process, and then discusses the relevant policies for the construction of photovoltaic power plants in the municipal sewage treatment plant. Analyze policy obstacles in the context of background. Secondly, in view of the policy that encourages the development of hydrogen energy at the national level but lacks specific and operable details, this report will also analyze the obstacles related to the policy system of hydrogen energy and fuel cell development. The overall goal of the report is to clarify policy obstacles for the distributed sewage treatment plant to coordinate solar photovoltaic power generation and electrolysis of hydrogen production, and to provide more policy guarantee suggestions for the further implementation and promotion of the project.

At present, the main source of hydrogen is carbon-based (gray hydrogen, hydrogen production from petrochemical energy). With the passage of time and technological development, its production will be more carbon-free or carbon-neutral (green hydrogen or blue hydrogen) hydrogen production technology Substitute. From a long-term perspective, zero-emission large-scale renewable energy hydrogen production methods will become the mainstream hydrogen

production methods in my country in the future, and many important progress have been made. Although the development of the hydrogen energy industry is in full swing, the top-level design of its hydrogen energy development policies is relatively lacking, and the hydrogen energy industry lacks specific policies to guide scientific development. Therefore, industry authorities should issue special plans as soon as possible to standardize and guide the approval process of hydrogen refueling stations and hydrogen production plants, and issue financial support policies for industrial development such as investment and operation of hydrogen energy infrastructure. Effective organization is also required. The coordinated and orderly competition of enterprises in the industrial chain, these related measures will play an important role in the sustainable development of the hydrogen production industry.

## **1. Analysis of relevant policy obstacles to the utilization of sewage as a resource**

Hydrogen production by water electrolysis uses water as raw material to produce hydrogen and oxygen through electrolysis. This technology has been widely used in chemical, metallurgy, building materials, electronics, aerospace and other fields. Since water electrolysis hydrogen production only uses water as raw material, does not require any chemical energy raw materials and gas sources, and there is no pollutant discharge in the process, and no "three wastes" are generated, so the layout is convenient and the construction threshold is low. At the same time, its safety and reliability are also higher than other hydrogen production methods. At present, the technology of hydrogen production by electrolysis of water mainly includes hydrogen production from alkaline water, hydrogen production from proton exchange membrane pure water, and hydrogen production from solid oxides. The most mature and popularized hydrogen production technology is alkaline water electrolysis. This project is based on the electrolysis of water hydrogen production coupled with photovoltaic power generation in the sewage treatment plant, and firstly faces the policy obstacles to the utilization of sewage resources. Therefore, this part of the report analyzes the policy obstacles in this regard.

### **Policy barriers:**

At the national level, the utilization of sewage as a resource is still in its preliminary stage, showing the characteristics of insufficient development and low utilization. At present, the discharge of urban sewage is about 75 billion cubic meters, while the utilization of recycled water is less than 10 billion cubic meters. The output and scale of recycled water need to be improved urgently. Currently, wastewater resource utilization mainly has the following problems: (1) Policies, regulations, management mechanisms and standard systems are not sound; (2) Reclaimed water utilization planning and facility construction with wastewater as the source are not coordinated; (3) Wastewater resource utilization Insufficient theoretical research and investment, and weak scientific and technological support. The utilization of sewage as a resource includes the utilization of

reclaimed water, resource recycling and energy conversion and utilization. On many issues such as its basic principles and main measures, overall research, overall planning, and coordinated advancement are required.

### **Obstacle analysis:**

In the early stage of the project, it is necessary to use alkaline water as the raw material for hydrogen production, but as the demand for hydrogen production gradually increases in the later stage, part of the reclaimed water will inevitably be introduced as the raw material for hydrogen production, which also provides a way to use the reclaimed water from the sewage treatment plant. However, my country does not yet have a law or regulation on the reuse of reclaimed water to clarify the application scope and use occasions of reclaimed water. However, the current general regulations come from water-saving departments, and their enforcement is far from sufficient. Therefore, the support and constraints of mandatory national laws and regulations are necessary. Specifically, they should include: new projects that can use reclaimed water should be planned, approved, and approved simultaneously. Design and construction; the water-saving department shall deduct the amount of alternative water available for reclaimed water when approving water use indicators to ensure the promotion of reclaimed water projects; units that have built reclaimed water facilities shall ensure their normal operation; The monitoring is regular and institutionalized.

In addition to compulsory promotion in laws and regulations, policy support should also be given. For the construction content of this project, the government can give priority to certain environmental protection project loans or give financial discounts, such as reducing or exempting value-added tax, income tax, and water capacity expansion fees for water production and utilization enterprises; for specific water reuse projects can be reduced or exempted Related municipal supporting fees, or free land use rights, etc., these favorable policies will promote the further development of the industry.

Among the many reasons for the imperfect system of reclaimed water reuse, the imperfect structure of water prices and the unscientific relationship between various water prices are some of the main reasons. For a long time, our country has the habit of emphasizing open source, neglecting expenditure and neglecting

reuse in the management of water resources. Residents pay lower water fees for a long time, the public is not very aware of water saving, and water resources are wasted seriously. Only when the price of reclaimed water is significantly lower than that of surface water and groundwater, that is to say, the public has a profit in the process of reusing reclaimed water, will the price leverage of reclaimed water price be brought into play and can guide reasonable water consumption. Therefore, formulate a reasonable price ratio relationship between surface water, groundwater, tap water, and reclaimed water, improve water resource utilization efficiency, rely on price measures to promote the formation of a reclaimed water utilization market, and promote the industrial development of reclaimed water reuse. To achieve the purpose of saving water. However, a reasonable water price system can never be achieved by relying on a certain policy. It also needs to comprehensively consider political, economic, social and other factors, and gradually adjust it. At the same time, it needs to adopt subsidies, special funds and preferential policies to improve water The enterprises dealt with are given support.

Reference material: “Guiding Opinions on Promoting the Utilization of Wastewater Resources”.

## **2. Analysis of policy obstacles to solar power plant project construction**

Renewable energy power generation has strong volatility and seasonality, and there are problems such as abandonment or surplus power caused by the short-term failure of the grid to absorb the power output of wind and solar water power generation. Making full use of wind power, solar energy, and water energy as the source of water electrolysis hydrogen production, and developing water electrolysis hydrogen production according to local conditions will have broad development and application prospects. This part of renewable electricity can also play an important role in regulating and balancing the grid load. However, during the construction of photovoltaic power stations, there are many policy obstacles that need to be resolved urgently.

### **olicy barriers:**

1. Due to the restrictions of the state to optimize the management of subsidized projects, it may be difficult for the photovoltaic projects of sewage hydrogen production plants to enjoy state subsidies. The specific performance is:

(1) Project categories are difficult to clarify. Since 2019, new photovoltaic power generation projects that require state subsidies have been divided into the following five categories: a. Photovoltaic poverty alleviation projects, including those that have been included in the national photovoltaic poverty alleviation catalogue and national plans; b. Household photovoltaic: the owner's own Household natural person distributed photovoltaic projects; c. Ordinary photovoltaic power plants: photovoltaic power plants with an installed capacity of 6 MW and above; d. Industrial and commercial distributed photovoltaic power generation projects: on-site development, nearby utilization, and single-point grid-connected installed capacity is less than Various distributed photovoltaic power generation projects other than 6 MW household photovoltaics; e. Special projects or demonstration projects organized and implemented by the state, including photovoltaic power generation projects in demonstration provinces, demonstration areas, and demonstration cities with a clear construction scale by the state, and Supporting photovoltaic power generation projects across provinces

and regions for power transmission channels. At present, photovoltaic power generation can barely be classified into e and d, but there is no specific and completely corresponding category, and the identification process is not clear.

(2) It is difficult to implement classified management. According to the total annual subsidies for new projects determined by the state, except for clear national policies and regulations, ordinary photovoltaic power plants, industrial and commercial distributed photovoltaic power generation projects, and special projects and demonstration projects organized and implemented by the state (hereinafter referred to as ordinary photovoltaic projects) are all in principle. It is organized by the local government through competitive allocation methods such as bidding, and the state determines the list of subsidies by sorting according to the amount of subsidy. This has caused part of the photovoltaic power generation projects not to receive national policy subsidies, which has brought huge cost pressures to enterprises.

#### **Obstacle analysis:**

The total subsidy budget for new photovoltaic power generation projects in 2020 is 1.5 billion yuan, which is significantly reduced compared to the 3 billion yuan in 2019. As the state optimizes the management of subsidized projects, clarifies project categories, and implements classified management, projects that are not in the above five categories do not enjoy government subsidies. In the construction of the electrolysis water hydrogen production project in the municipal sewage treatment plant, it can be applied for certification as type d or e, but if the certification is unsuccessful, it is difficult for the project to enjoy state subsidies.

#### **Policy barriers:**

2. Strict early warning management. If the area where the photovoltaic project of the sewage hydrogen plant is located is red or orange, in principle, no new projects can be built.

Newly built photovoltaic power generation projects must comply with relevant national and regional planning, as well as management requirements such as market environmental monitoring and evaluation, and "first build, first serve"



is strictly prohibited. All provincial-level energy authorities should fully communicate with local provincial-level grid companies, calculate and demonstrate the grid connection and consumption conditions of the new installed capacity of photovoltaic power generation in their province-level regions, and organize project construction in an orderly manner. In areas where the monitoring and evaluation results are in red, in principle, no new projects will be arranged except for photovoltaic poverty alleviation projects, affordable on-grid demonstration projects that have been scheduled to be constructed, and transmission and consumption projects through inter-provincial and cross-regional transmission channels. For areas where the results of monitoring and evaluation are orange, it is necessary to rationally regulate and control new projects on the premise that safeguard measures to effectively improve the market environment are put forward. In areas where the results of monitoring and evaluation are green, project construction can be promoted in an orderly manner on the basis of the implementation of the conditions for connection and elimination. Newly built photovoltaic power generation projects in Tibet are managed by the autonomous region in accordance with the management requirements for the consumption of all electric power in the region, monitoring and early warning, etc.

Obstacle analysis: According to this regulation, in areas where the monitoring and evaluation results are red, new photovoltaic projects cannot be built, and most of the construction sites of this project are sewage treatment plants. It is possible that the monitoring and evaluation results are red. This requires the government to re-evaluate the overall project. The economic and social benefits and environmental benefits of the project should be considered comprehensively. If only rigidly complying with the principle of "red and orange, in principle, no new projects can be built", the development of the new model of photovoltaic power generation coupled with electrolysis of water for hydrogen production will be inhibited to a large extent.

Reference materials: "Notice of the National Energy Administration on matters related to the construction of wind power and photovoltaic power generation projects in 2019", "Notice of the National Energy Administration on matters related to the construction of wind power and photovoltaic power

generation projects in 2020”.

### **3. Analysis of policy obstacles to the establishment of electrolysis water hydrogen production plants**

Hydrogen energy is a clean and efficient secondary energy source that can be stored for a long time and can be transported over long distances through pipelines. It can not only be directly used for large-scale power generation, but also can be used in a large number of industrial productions. At present, fossil energy is depleted day by day, environmental pollution pressure is increasing day by day, coupled with the increasingly severe carbon emission problem, it is foreseeable that hydrogen energy will play an increasingly important role in the future. Hydrogen production by electrolysis of water is a good technical route for hydrogen production. Combining the production of hydrogen by electrolysis of water and the technical route of adjusting the grid connection can use surplus electricity from renewable energy sources to electrolyze water to produce hydrogen, which greatly improves Renewable energy utilization efficiency. In order to control the quality of power generation and meet the requirements of power grid peak shaving, the renewable energy power generation system needs to use brakes or other system adjustment actions. The intervention of the electrolysis hydrogen production system can greatly reduce these actions, thereby reducing the operation and maintenance of the power generation system. cost. Hydrogen production from electrolysis of water is currently the most ideal application model for renewable energy power generation. However, in addition to complicated procedures, the establishment of a hydrogen production plant also faces a series of policy obstacles.

#### **Policy barrier 1:**

The hydrogen plant is a hazardous chemical production enterprise, and its location and layout and planning and design shall comply with the “Regulations on the Safety Management of Hazardous Chemicals” (Order No. 591 of the State Council) and the “Measures for the Implementation of Safety Production Permits for Hazardous Chemicals Production Enterprises” (formerly State Administration of Work Safety Order No. 41) and other relevant laws, regulations, and standards

and specifications, meet the requirements of safe production, and obtain a safe production license in accordance with the law. According to the “Technical Specifications for Hydrogen Refueling Stations” (GB50516-2010) issued by the Ministry of Housing and Urban-Rural Development and the former General Administration of Quality Supervision, Inspection and Quarantine of the People’s Republic of China, hydrogen refueling stations refer to “hydrogen storage for hydrogen energy vehicles or hydrogen internal combustion engine vehicles or hydrogen and natural gas hybrid vehicles. “Special places for filling hydrogen fuel in bottles” are similar in nature to LNG refueling stations commonly used in China.

According to the "Regulations on the Safety Management of Hazardous Chemicals", the establishment of a hydrogen production plant needs to meet at least the following conditions:

#### Chapter Two: Production and Storage Safety

Article 12: New, rebuilt, expanded construction projects (hereinafter referred to as construction projects) for the production and storage of hazardous chemicals shall be reviewed by the safety production supervision and management department.

The construction unit shall conduct a safety condition demonstration for the construction project, entrust an organization with the qualifications prescribed by the state to conduct a safety evaluation on the construction project, and report the safety condition demonstration and safety evaluation to the people's government at or above the districted city level where the construction project is located The work safety supervision and management department; the work safety supervision and management department shall make a review decision within 45 days from the date of receipt of the report and notify the construction unit in writing. The specific measures shall be formulated by the work safety supervision and administration department of the State Council.

Article 13: Units that produce and store hazardous chemicals shall set up obvious signs on the hazardous chemical pipelines they have laid, and shall inspect and test the hazardous chemical pipelines on a regular basis.

For construction operations that may endanger the safety of dangerous chemical pipelines, the construction unit shall notify the pipeline unit in writing

7 days before the start of construction, and jointly formulate an emergency plan with the pipeline unit and take corresponding safety protection measures. The unit to which the pipeline belongs shall assign special personnel to the site to provide guidance on pipeline safety protection.

Article 14: Before carrying out production, a hazardous chemical production enterprise shall obtain a hazardous chemical production safety license in accordance with the provisions of the "Safety Production License Regulations.

Enterprises that produce hazardous chemicals listed in the catalogue of industrial products under the national production license system shall obtain industrial product production licenses in accordance with the "Regulations of the People's Republic of China on the Administration of Industrial Product Production Licenses.

Article 16: Enterprises producing hazardous chemicals subject to key environmental management shall, in accordance with the provisions of the environmental protection department of the State Council, report the release of such hazardous chemicals into the environment and other relevant information to the environmental protection department. The competent department of environmental protection may take corresponding environmental risk control measures according to the situation.

Article 20: Units that produce and store hazardous chemicals shall, according to the types and hazardous characteristics of the hazardous chemicals they produce and store, set up corresponding monitoring, monitoring, ventilation, sun protection, temperature regulation, fire prevention, fire extinguishing, Safety facilities and equipment such as explosion-proof, pressure relief, anti-virus, neutralization, moisture-proof, lightning protection, anti-static, anti-corrosion, anti-leakage, and protection of dikes or isolation operations, and the safety facilities, The equipment is regularly maintained and maintained to ensure the normal use of safety facilities and equipment.

Units that produce and store hazardous chemicals shall set up obvious safety warning signs on their work sites and safety facilities and equipment.

### **Obstacle analysis:**

Hydrogen production from electrolysis of water belongs to the production of

hazardous chemicals and shall comply with the provisions of the Regulations on Safety Management of Hazardous Chemicals. First of all, the production should be reviewed by the safety production supervision and management department. Secondly, it should set up obvious signs for the dangerous chemical pipelines laid, and regularly inspect and test the dangerous chemical pipelines; it should obtain the dangerous chemical safety production license in accordance with the provisions of the "Safety Production License Regulations". Finally, it is necessary to report to the environmental protection department and conduct real-time monitoring at the production site. The qualification process for electrolysis of hydrogen production involves multiple departments, and it takes a lot of time to apply and declare.

### **Policy barrier 2:**

According to the "Measures for the Implementation of Safety Production Permits for Hazardous Chemicals Production Enterprises", hydrogen production enterprises need to apply for safe production permits.

#### **Chapter II     Conditions for Applying for a Work Safety License**

Article 8 :    The location and layout, planning and design of the enterprise, and the distance from important places, facilities, and areas shall meet the following requirements:

(1) National industrial policy; planning and layout of local people's governments at or above the county level (including county level); newly established enterprises are built in areas specially used for the production and storage of hazardous chemicals planned by the local people's government.

(2) Dangerous chemical production installations or storage facilities that store hazardous chemicals in quantities that constitute a major source of hazard shall be in compliance with the distance between the eight types of places, facilities, and areas specified in Article 19, paragraph 1 of the "Hazardous Chemical Safety Management Regulations" Relevant laws, regulations, rules and national standards or industry standards.

(3) The overall layout meets the requirements of the "Code for General Layout and Transportation Design of Chemical Enterprises" (GB50489), "Code for General Layout Design of Industrial Enterprises" (GB50187), and "Code for

Fire Protection Design of Buildings” (GB50016).

Article 9: The factory buildings, operating sites, storage facilities and safety facilities, equipment, and processes of an enterprise shall meet the following requirements:

(1) Newly built, rebuilt, and expanded construction projects are designed, manufactured, and constructed by a unit with qualifications prescribed by the state; devices involving hazardous chemical processes and key supervision of hazardous chemicals shall be designed by a comprehensive Class A qualification or a chemical and petrochemical professional Designed by qualified chemical and petrochemical design unit.

(2) Processes and equipment that are explicitly eliminated, prohibited by the state, and endanger safe production shall not be adopted; newly developed production processes for hazardous chemicals must be gradually scaled up to industrial production on the basis of small-scale, pilot-scale, and industrialized tests; domestic first use the chemical process must undergo a safety and reliability demonstration organized by the relevant departments of the provincial people’s government.

(3) Installation of automated control systems for installations involving hazardous chemical processes and key supervision of hazardous chemicals; installation of emergency shutdown systems for large-scale chemical installations involving hazardous chemical processes; installation of sites involving flammable, explosive, toxic and hazardous chemicals Inflammable, explosive, toxic and harmful media leakage alarm and other safety facilities.

(4) The production area is set up separately from the non-production area and meets the distance specified by the national standard or industry standard.

(5) The distance between the production equipment and storage facilities of hazardous chemicals and the distance from the buildings (structures) shall comply with the relevant standards and regulations. The arrangement of equipment, facilities and buildings (structures) in the same plant area must be subject to the provisions of the same standard.

### Chapter III Application for Work Safety License

Article 23: Central enterprises and their directly controlled enterprises (headquarters) involved in the production of hazardous chemicals shall apply to

the State Administration of Work Safety for a production safety license.

Enterprises other than those specified in the first paragraph of this article shall apply to the local provincial safety production supervision and administration department or the safety production supervision and administration department entrusted by them for a safety production license.

Article 24: An application for a safety production license for a newly-built enterprise shall be submitted within 10 working days from the date when the safety facilities of the hazardous chemical production and construction project pass the acceptance check.

Article 25: When an enterprise applies for a production safety license, it shall submit the following documents and materials and be responsible for the authenticity of their contents:

(1) Documents and application form for applying for a production safety license;

(2) Work safety responsibility system documents, work safety rules and regulations, and a list of post operation safety regulations;

(3) Setting up a production safety management agency, and assigning copies of documents of full-time production safety management personnel;

(4) A copy of the safety qualification certificate or special operation operation certificate of the main person in charge, the person in charge of safety, the safety production manager, and the special operation personnel;

(5) Reports on the withdrawal and use of expenses related to production safety, and the newly-built enterprise submits documents related to the withdrawal and use of safe production expenses;

(6) Proof of paying work-related injury insurance premiums for employees;

(7) Recording certification documents of emergency rescue plans for hazardous chemical accidents;

(8) A copy of the hazardous chemical registration certificate;

(9) A copy of the industrial and commercial business license or a copy of the industrial and commercial approval document;

(10) A safety evaluation report issued by a qualified intermediary agency;

(11) A copy of the completion acceptance letter of the newly-built enterprise;

(12) List of emergency rescue organizations or emergency rescue personnel,



as well as emergency rescue equipment, equipment and facilities.

An enterprise with a major hazard source of hazardous chemicals shall, in addition to submitting the documents and materials specified in the first paragraph of this article, also submit the filing certification documents and materials of the major hazard source and its emergency response plan.

**Obstacle analysis:**

Hydrogen production from electrolysis of water belongs to the production of hazardous chemicals, and a safety production license should be applied for in accordance with the relevant regulations of the hazardous chemical production enterprise. The specific requirements include the location and layout of the company, planning and design, and distance requirements from important places, facilities, and regions. Make certain requirements for the company's factory buildings, workplaces, storage facilities and safety facilities, equipment, and processes. To apply for a permit, all the above-mentioned materials should be prepared. Therefore, the application process is complicated, time-consuming, and involves many departments.

Reference materials: Ministry of Emergency Management “Response to Recommendation No. 4620 of the First Session of the Thirteenth National People's Congress—Emergency Jianhan [2018] No. 16”, “Regulations on Safety Management of Hazardous Chemicals”, “Safety Production License for Hazardous Chemicals Production Enterprises Measures for the Implementation of Certificates”.

## **4. Analysis of Policy Obstacles to the Construction of Hydrogen Refueling Stations**

At present, only Hainan Province has the approval process (trial) method for the construction of hydrogen refueling stations in China, and there is no documented construction approval process in other regions. This will result in the lack of sufficient legal and policy basis for the establishment of hydrogen refueling stations. The construction of hydrogen refueling stations may encounter many policy problems and the construction process will be slow.

The Hainan Provincial Department of Housing and Urban-Rural Development, Hainan Provincial Department of Transportation, Hainan Provincial Department of Natural Resources and Planning, Hainan Provincial Department of Ecological Environment, Hainan Provincial Market Supervision and Administration, Hainan Provincial Meteorological Bureau, Hainan Provincial Committee of the Communist Party of China The office jointly issued the notice of the “Hainan Hydrogen Refueling Station Construction Approval Process (Trial)”. It is known that before the approval of the hydrogen refueling station project, the opinions of the competent department of the hydrogen refueling station industry selected by the county government should be sought in advance. The notice specifically pointed out that hydrogen refueling station projects in expressway service areas and port areas and supporting hydrogen refueling station projects involving bus route planning should seek advice from the transportation department.

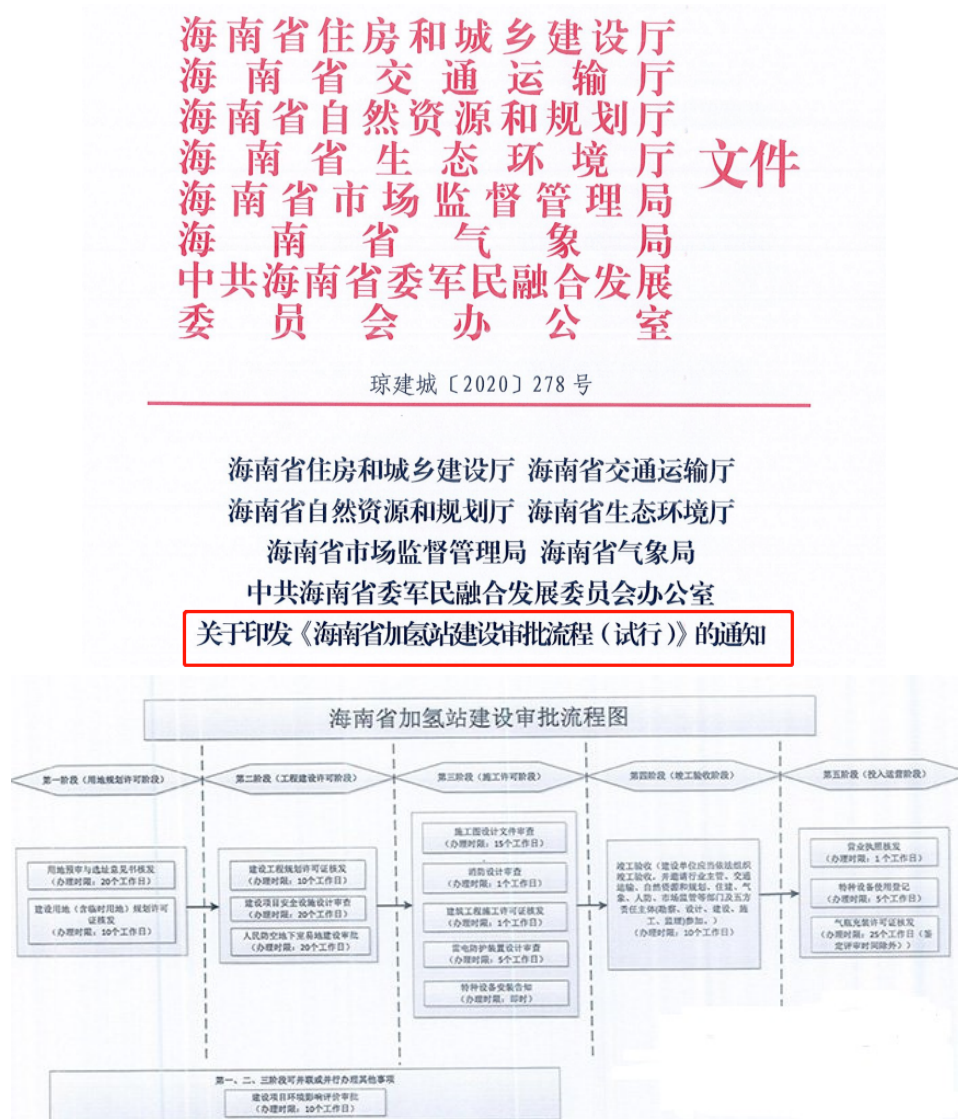


Figure 3.1 Screenshot of relevant policies and regulations

According to the document, the approval of the hydrogen refueling station project in Hainan Province is divided into 5 stages, the specific contents are as follows

(1) Land use planning permission stage

1. Pre-examination of land use and issuance of site selection opinions. According to the “Notice of the Hainan Provincial Department of Natural Resources and Planning on Doing a Good Job in the Reform of "Multiple Audits and Multiple Certificates" for Planned Land Use” (Qiong Natural Resources Letter [2020] No. 227), pre-examination of land use and site selection opinions are required In case of a certificate, an application shall be made to the natural resources and planning department, and the natural resources and planning department will issue corresponding documents. (Time limit for processing: 20

working days) The construction of hydrogen refueling stations involving foreign operations should meet the relevant planning requirements. The supporting hydrogen refueling station involved in the enterprise's own use shall not be operated externally, and the enterprise's own land can be used as project land.

2. Issuance of planning permits for construction land (including temporary land use). Apply to the natural resources and planning department, and the natural resources and planning department will issue corresponding documents. (Time limit for processing: 10 working days)

(2) Project construction permit stage

1. Issuance of construction project planning permit. Apply to the natural resources and planning department, and submit relevant land certificates, construction project design plans, etc. Project construction engineering design plans that have been reviewed and meet the requirements of relevant laws, regulations and technical specifications, and do not involve new construction, expansion, and reconstruction of buildings, structures, roads, pipelines and other engineering facilities, are exempt from applying for construction engineering planning permits. (Time limit for processing: 10 working days)

2. Design review of safety facilities for construction projects. Apply to the safety production supervision and management department, and the safety production supervision and management department will issue the corresponding repudiation documents. (Time limit for processing: 20 working days)

3. Examination and approval of the construction of the civil air defense basement. Apply to the competent department of civil air defense, and the competent department of civil air defense will issue corresponding approval documents. (Time limit for processing: 20 working days)

((3) Construction permit stage

1. Review of construction drawings and design documents. A qualified professional institution is entrusted to conduct the review, and the professional institution will issue a review opinion. (Time limit for processing: 15 working days)

2. Fire protection design review. Apply to the housing construction department, and the housing construction department will issue corresponding review documents. (Time limit for processing: 1 working day)

3. Issuance of construction permits for construction projects. Apply to the housing and construction department. Before the relevant laws and regulations of the hydrogenation station industry are promulgated and implemented, the construction of the hydrogen refueling station will not implement the construction permit notification and commitment system for approval. (Time limit for processing: 1 working day)

4. Design review of lightning protection device. Apply to the Meteorological Department, and the Meteorological Department will issue corresponding review documents. (Time limit for processing: 5 working days)

5. Special equipment installation notice. Construction units with special equipment installation qualifications shall inform the special equipment safety supervision and management department of the special equipment to be installed on the special equipment supervision system website before construction. (Time limit for processing: Immediately)

6. Approval of environmental impact assessment of construction projects. Submit an application to an approval agency with the authority to approve the environmental assessment of construction projects, and the approval document will be issued by it. (Time limit for processing: 10 working days)

#### (4) Completion acceptance stage

The construction unit shall organize the completion acceptance in accordance with the law, and invite industry supervisors, transportation, natural resources and planning, housing construction, meteorology, civil air defense, market supervision and other departments, as well as the five parties' responsibility subjects (reconnaissance, design, construction, construction, supervision) to participate. (Time limit for processing: 10 working days)

Within 15 days, the construction unit shall submit the following project data to the industry competent department selected by the city and county government:

Project filing documents, planning, fire protection, civil air defense, and meteorological departments' approval documents;

Project archives of hydrogen refueling station construction, survey, design, construction, and supervision units;

Other files.

#### (5) Put into operation stage

1. Issuance of business license. Apply to the market supervision department. Before the relevant laws and regulations clearly stipulate the operation and management of the hydrogen refueling station, the hydrogen refueling station business unit does not need to apply for the business license, and the market supervision department shall not use the business license as a prerequisite for the business license condition. (Time limit for processing: 1 working day)

2. Registration for the use of special equipment. The application to the market supervision department shall be handled by the market supervision department in accordance with the "Special Equipment Use Management Rules" and other relevant regulations. (Time limit for processing: 5 working days)

3. The gas cylinder filling permit is issued. Apply to the market supervision department, which will be handled by the market supervision department in accordance with the "Special Equipment Safety Law of the People's Republic of China", "Special Equipment Production and Filling Unit Licensing Rules" (TSG07-2019) and other relevant regulations. (Time limit for processing: 25 working days (except appraisal review time))

#### **Obstacle analysis:**

It can be seen that although there are written regulations and policies, there are many departments involved in the process, the procedures are complicated, and the process takes a long time. Hydrogen refueling station construction not only has specific requirements for site selection, but also requires project construction to apply for approval in advance from relevant departments. At the same time, it also requires review of drawings, fire protection, etc., and the operation of hydrogen refueling stations also requires the issuance of business licenses and the use of special equipment. Registration, gas cylinder filling permit issuance and other procedures. In short, the approval process for the construction of hydrogen refueling stations is very cumbersome and time-consuming.

Reference materials: "Hainan Province Hydrogen Refueling Station Construction Approval Process (Trial) Issuance"

## **5. Analysis of Policy Obstacles to Fuel Cell Utilization**

The hydrogen energy produced by the project can firstly meet the electricity demand of the sewage plant itself, and secondly meet the electricity demand of the hydrogen production power source of the plant, and the excess hydrogen will be transferred to the hydrogen refueling station for further use. One of the important destinations of hydrogen in hydrogen refueling stations is the new type of hydrogen fuel cell for vehicles. In the process of fuel cell preparation, the high cost of fuel cell system hinders the marketization of fuel cell applications. This is mainly due to the high technical barriers and high costs of proton exchange membranes that make up the fuel cell system, the use of precious metal platinum as the catalyst, and the processing of bipolar plates. It is caused by high cost and other issues under strict craftsmanship. But at the same time, the lack of relevant systems and incentive measures is also an important reason for restricting its development. The specific manifestations are as follows:

### **Policy barriers:**

The Ministry of Finance, Ministry of Industry and Information Technology, Ministry of Science and Technology, Development and Reform Commission, and National Energy Administration recently officially jointly issued the “Notice on Carrying out Fuel Cell Vehicle Demonstration Application” (hereinafter referred to as the “Notice”), which clearly stated that during the demonstration period, the five departments will Adopt the method of "reward for compensation", and reward the city groups shortlisted for demonstration in accordance with their goal completion.

The general idea of the “Notice” is to support breakthroughs in key core technologies and industrial applications of fuel cell vehicles, and promote the formation of a fuel cell development pattern with a reasonable layout, different priorities and coordinated advancement. However, in the absence of relevant stimulus policies specifically for fuel cells, the phenomenon of heavy thunder and small raindrops has appeared to a large extent.

### **Obstacle analysis:**

The current established policies generally target fuel cell vehicles, and few policies directly target the fuel cell itself. We believe that the government should first focus on supporting R&D breakthroughs in key core technologies in the fuel cell field, and promote the process of evaluation, verification and iterative improvement of key components in industrial applications. The second is to focus on supporting fuel cell demonstration applications. For example, this project can be used as a sample of demonstration applications; again, effective business operation models should be explored to improve the economy of fuel cells, and the demonstration city clusters should focus on advantageous companies.



## **6. Summary**

This report focuses on the use of renewable energy in urban sewage treatment plants to build hydrogen production from electrolyzed water, and analyzes the policy obstacles they may encounter. The content covers the reuse of sewage resources, the construction of solar photovoltaic power plants, the establishment of hydrogen production plants, there are five major obstacles to the construction of hydrogen refueling stations and the application of fuel cells. This report will clarify the policy barriers for the coordinated coupling of solar photovoltaic power generation and electrolyzed hydrogen production in distributed sewage treatment plants, and provide policy guarantee suggestions for the further implementation and promotion of the project, which has a positive reference role.

## Chapter IV Conclusion and Outlook

The high dependence on energy imports has become a huge hidden danger to China's energy security. As a secondary energy source with a wide range of sources, green and efficient, hydrogen will surely become an important part of China's energy system in the future, helping to improve some of the problems in China's energy status. At the same time, each link of hydrogen production, hydrogen storage, and hydrogen use can generate huge commercial and social value, which is of great significance to China's industrial upgrading and sustainable economic development. From the current point of view, the utilization of domestic chemical by-product hydrogen is a better choice for hydrogen supply in the fuel cell industry. The domestic chlor-alkali, PDH and fast-developing ethane cracking industries can provide sufficient low-cost hydrogen resources, and they are concentrated in the load center. In the dense East China region, after low-intensity transformation, it can simultaneously solve the problem of whether the hydrogen supply and by-product hydrogen in the fuel cell industry can be used efficiently. In the future, centralized hydrogen supply by chemical by-products and decentralized hydrogen production by water electrolysis will be used. This will be the main development trend of the hydrogen supply model of the domestic fuel cell industry.

First of all, this report aims to study the carbon emissions and cost analysis of the electrolytic alkaline water hydrogen production system during the 25-year life cycle. It uses inventory analysis and uses SimaPro9 software and the IPCC 2013 impact assessment method to simulate electrolytic alkaline water production. Hydrogen system. Through case studies, life cycle assessments are carried out from two aspects: the construction phase and the operation phase of the electrolysis alkaline water hydrogen production system within the 25-year life cycle. In terms of overall environmental impact, the carbon emissions of the electrolysis hydrogen production system during the 25-year life cycle It is  $-3.84 \times 10^7$  kg CO<sub>2</sub> eq. The operation stage has the greatest impact on the environment, indirectly reducing the emissions of  $4.28 \times 10^7$  kg CO<sub>2</sub> eq. The electrolysis of alkaline water hydrogen production system will only produce carbon emissions during the construction phase. The source of carbon emissions

is mainly the production of polysilicon batteries, which account for 63% of carbon emissions during the construction phase. In order to improve the environmental benefits of the system, the production process of polycrystalline silicon cells can be improved to reduce carbon emissions during the production process. The total investment of this project is estimated to be 28.02 million yuan, including initial system construction and equipment investment costs totaling 24.15 million yuan and 25-year operating costs totaling 3.87 million yuan. The total hydrogen production of the project in 25 years is 1013.9 tons. The hydrogen will be sold directly. The total income of the project in 25 years is 65.9 million yuan. Through calculation and analysis, this project will achieve a return in the tenth year, with a return on investment of 2.35%. In order to evaluate the environmental and economic benefits of the project, the economic net present value is used for evaluation. The economic net present value of the project is 209, which is greater than zero. Therefore, it is considered that the project has a large net contribution to the national economy during its life cycle and is an investment project that can be considered.

Secondly, this report analyzes the problems of policies, regulations, management mechanisms, and standard systems that exist in the wastewater resource utilization during the construction of sewage plants, and then specifically discusses the relevant policies for the construction of photovoltaic power plants in urban sewage treatment plants and discusses Analysis of policy obstacles in the context of the entire context. Secondly, in view of the policy that encourages the development of hydrogen energy at the national level but lacks specific and operable details, this report will also analyze the obstacles related to the policy system of hydrogen energy and fuel cell development. The overall goal of the report is to clarify policy obstacles for the distributed sewage treatment plant to coordinate solar photovoltaic power generation and electrolysis of hydrogen production, and to provide more policy guarantee suggestions for the further implementation and promotion of the project.

At present, the main source of hydrogen is carbon-based (gray hydrogen, hydrogen production from petrochemical energy). With the passage of time and technological development, its production will be more carbon-free or carbon-neutral (green hydrogen or blue hydrogen) hydrogen production technology

Substitute. From a long-term perspective, zero-emission large-scale renewable energy hydrogen production methods will become the mainstream hydrogen production methods in my country in the future, and many important progress have been made. Although the development of the hydrogen energy industry is in full swing, the top-level design of its hydrogen energy development policies is relatively lacking, and the hydrogen energy industry lacks specific policies to guide scientific development. Therefore, industry authorities should issue special plans as soon as possible to standardize and guide the approval process of hydrogen refueling stations and hydrogen production plants, and issue financial support policies for industrial development such as investment and operation of hydrogen energy infrastructure. Effective organization is also required. The coordinated and orderly competition of enterprises in the industrial chain, these related measures will play an important role in the sustainable development of the hydrogen production industry.