Technical Research on Hydrogen Supply Chain Industry

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Abstract. This article compares different types of hydrogen production technology, and it is not advisable to decide which hydrogen production method to use based solely on the production cost of the technology. It is also necessary to consider the local resource situation. The central and western regions are rich in hydropower and natural gas resources, and the prices are relatively low. The natural gas reforming hydrogen production plus distributed electrolysis water hydrogen production technology is a recoverable solution; there are many chemical and iron and steel enterprises in the eastern coast and the Bohai Rim region, and the industrial by-product hydrogen purification technology is a better choice; there are abundant renewable resources such as photovoltaic and wind energy in Northeast, North China, and Northwest, and can use renewable energy electrolytic hydrogen production technology; Inner Mongolia, Shanxi, Shaanxi and other places have excellent coal resources, and the potential of coal hydrogen production technology is huge. The establishment of the layout of the downstream hydrogen refuelling station and the establishment of the application market are also crucial to the upstream hydrogen production enterprises. Areas where the front-end hydrogen production link and the back-end application link are well integrated can gain a favourable position.

1. Introduction
The high cost of hydrogen production is one of the main obstacles to restrict the promotion of hydrogen energy: through disassembly and comparison with the use cost of other types of cars on the market, excessive fuel consumption costs are one of the sources that cause the overall cost of fuel cell vehicles to be high. Compared with other industries, hydrogen's higher fuel prices mainly come from production and preparation. From the perspective of my country's current hydrogen infrastructure improvement and technical level, the cost of hydrogen including hydrogen production and storage and transportation accounts for about 70% of the terminal price of hydrogen refueling stations, of which the cost of hydrogen raw materials accounts for 50%. Therefore, the hydrogen production link largely determines the economics of using hydrogen fuel[1-2].

The clean hydrogen resources that can be used for hydrogen supply in fuel cell vehicles are considerable, but they face the problem of insufficient market competitiveness: domestic hydrogen production resources are abundant, and alternative hydrogen production pathways are also more diverse. If hydrogen is produced by electrolyzing water, more than 2 million tons of clean hydrogen can be produced, which is enough to meet the needs of the hydrogen industry in the short to medium term. However, the economics of various types of hydrogen production routes are not enough to ensure the large-scale commercialization of fuel cell vehicles. Coupled with the current constraints of hydrogen
storage and transportation, the hydrogen transportation bottleneck has not yet been completely broken through and the cost is relatively high. Under the current hydrogen supply system, the cost of hydrogen including production, storage and transportation is not competitive in the market[3-4].

Hydrogen by-product from chemical industry is the current transition plan, and hydrogen production from natural gas reforming is relatively mature, and it is also the mainstream hydrogen production method abroad. However, natural gas raw materials account for more than 70% of the cost of hydrogen production, which is not in line with China's resource endowment of coal-rich, lean oil, and low gas; the theoretical scale of coke oven gas hydrogen production is huge, and the domestic coke output reached 430 million tons in 2018. The hydrogen content in coal gas accounts for about 50-60%, and can produce more than 7 million tons of by-product hydrogen, which is extremely large, accounting for more than 90% of the total amount of industrial by-product hydrogen, but it is difficult to control the purification of trace impurities in the product hydrogen. Chemicals, especially chlor-alkali chemicals and other by-product hydrogen, have high purity. The annual output of caustic soda in China is basically stable at 30-35 million tons, and by-product hydrogen is 750-875,000 tons. After deducting about 60% of the hydrogen, it is used by supporting polyvinyl chloride and hydrochloric acid, The remaining about 28-34 million tons. The hydrogen content of methanol, synthetic ammonia, and PDH synthesis gas is between 60-95%, which can meet the requirements of fuel cells after purification. China's PDH projects have been built and are under construction. The by-product hydrogen content is about 370,000 tons/year; China's synthetic ammonia production capacity is 150 million tons/year, and the recoverable hydrogen is about 1 million tons/year; a total of 1.68 million tons/year. According to 3.8kg hydrogen consumption per 100 kilometers, each vehicle runs 20,000km annually, which can meet the demand of 2.2 million fuel cell vehicles, and can meet the development roadmap of hydrogen energy and fuel cell in China. Requirements, but due to carbon emissions, it does not comply with the concept of green development. In the long run, the realization of hydrogen production from renewable energy is the ultimate solution.

2. Hydrogen production from fossil energy

2.1. Coal hydrogen production process
Coal is the main raw material for hydrogen production in my country. Although coke oven gas by-produced by coal coking is also used for hydrogen production, coal gasification hydrogen production currently occupies a dominant position in domestic hydrogen production. Coal gasification produces hydrogen by first reacting coal with oxygen and then reacting with water to obtain gaseous products with hydrogen and CO as the main components. After desulfurization and purification, CO continues to undergo a shift reaction with water vapor to generate more hydrogen. Finally, after separation, purification and other processes, a certain purity of product hydrogen is obtained. The process of coal gasification hydrogen production technology generally includes the main production links such as coal gasification, coal gas purification, CO shift and hydrogen purification[5].

Hydrogen production from coal has a long history and mature technology. It is a raw material for the preparation of various products such as synthetic ammonia, methanol, liquid fuel, and natural gas. It is widely used in coal chemical industry, petrochemical, steel and other fields. For decades, the chemical and fertilizer industries have been using this technology to produce ammonia (especially in China). There are about 130 coal gasification plants in operation worldwide, of which more than 80% are in China. The hydrogen production technology of coal is mature and efficient, and can be prepared on a large scale and stable. It is currently the lowest cost hydrogen production method. According to IEA data, capital expenditure accounts for about 50% of the cost of coal gasification to produce hydrogen, and fuel demand accounts for 15-20%. Therefore, the availability and cost of coal play an important role in determining the feasibility of coal-to-hydrogen projects. According to the calculation of China Hydrogen Energy Alliance, taking the coal gasification technology with mature technology and lower cost as an example, the device with an annual production capacity of 540,000 cubic meters of synthesis gas will cost 600 yuan for raw coal (6000 kcal, more than 80% carbon content). In the case of tons, the cost of producing hydrogen is about 8.85 yuan/kg[6].
The carbon dioxide emissions from the coal-to-hydrogen process are about four times that of natural gas-to-hydrogen, which needs to be combined with carbon capture and storage (CCS) technology to reduce emissions. According to IEA data, the addition of CCS to coal-to-hydrogen production is expected to increase capital expenditures and fuel costs by 5% and 130%, respectively. The China Hydrogen Energy Alliance calculated that the cost of coal-to-hydrogen production will increase to approximately RMB 15.85 per kg after adding CCS on the aforementioned basis. As a large coal country, China is rich in coal resources and has a lot of coal mining infrastructure. Due to the lack of cheap natural gas sources in China, a coal-to-hydrogen process equipped with CCS is likely to be the cheapest option for clean hydrogen production at least in the medium term.

2.2. Natural gas hydrogen production process

The technology is mainly divided into three types according to the different oxidant properties:

1. Steam reforming: pure steam is used as an oxidant, and the reaction needs to absorb heat;
2. Partial oxidation: using oxygen or air, exothermic reaction process;
3. Autothermal reforming: a combination of steam reforming and partial oxidation, mixing air and water vapor, and adjusting the ratio of the two oxidants so that it does not need to absorb or emit heat (isothermal).

Methane steam reforming (SMR) is currently the most extensive technology for natural gas large-scale hydrogen production. Reforming is the conversion of hydrocarbons and alcohols to hydrogen through a chemical process under catalyst conditions, producing by-products water (steam), carbon monoxide and carbon dioxide. The reaction temperature is approximately between 700°C and 900°C. In the short term, SMR will remain the dominant technology for large-scale hydrogen production because of its better economic benefits and the large number of SMR devices in operation worldwide.

The natural gas hydrogen production process mainly includes four processes: raw gas pretreatment, natural gas steam conversion, carbon monoxide conversion, and hydrogen purification. The first is the raw material pretreatment, which mainly refers to the raw material gas desulfurization. In the actual process operation, natural gas cobalt molybdenum hydrogenation tandem zinc oxide is generally used as a desulfurizing agent to convert organic sulfur in natural gas into inorganic sulfur for removal. The second is to carry out steam reforming of natural gas, using nickel-based catalysts in the reformer to convert alkanes in natural gas into feed gas containing carbon monoxide and hydrogen as the main components. Then there is carbon monoxide shift, which reacts with water vapor in the presence of a catalyst, thereby generating hydrogen and carbon dioxide, and obtaining a shift gas whose main components are hydrogen and carbon dioxide. The last step is to purify hydrogen. One of the most commonly used hydrogen purification systems is the pressure swing adsorption purification separation (PAS) system. This system has low energy consumption, simple process, and high purity of hydrogen. Up to 99.99%.

The cost of natural gas hydrogen production is affected by various technical and economic factors, of which natural gas prices and capital expenditures are the two most important factors. Fuel cost is the largest cost component, accounting for 45-75% of production costs in different countries and regions. Natural gas prices are lower in the Middle East, Russia and North America, so hydrogen production costs are also the lowest. Natural gas importing countries such as China are faced with higher natural gas import prices, resulting in higher hydrogen production costs. According to the China Hydrogen Energy Alliance, domestic natural gas raw materials account for more than 70% of the cost of hydrogen production, and the price of natural gas is an important factor in determining the price of hydrogen production. And considering that carbon emission treatment needs to be combined with CCUS technology, it will result in an average capital expenditure increase of about 50% and a fuel cost increase of about 10%. Due to the transportation and storage costs of carbon dioxide, the average operating cost has also doubled. Considering the resource endowment conditions of China's "oil shortage and gas shortage", only a few regions with rich natural gas resources such as the Midwest can explore this hydrogen production path.
3. Industrial by-product hydrogen

People's increasing interest in the by-product hydrogen in industrial production can be traced back to the 1980s, when the number of vehicles driven by fuel cells gradually increased, and the feasibility of using hydrogen as a transportation fuel became increasingly fierce. Some studies have evaluated the potential of using industrial by-product hydrogen for early demonstration of fuel cell vehicles. By-product hydrogen can be used as an entry point before hydrogen is widely used in renewable energy production. Moreover, the distributed industrial infrastructure can also be regarded as the foundation or stepping stone of the universal hydrogen supply system. Industrial by-product hydrogen is mainly distributed in steel, chemical and other industries. The main sources include coke oven gas hydrogen production, chlor-alkali by-product hydrogen production, and light hydrocarbon cracking by-product hydrogen production. Purification and utilization of hydrogen can not only improve resource utilization efficiency and economic benefits, but also reduce pollution and improve the environment.

3.1. Coke oven gas hydrogen production process

China is the world's largest coke producer. In 2018, domestic coke production reached 430 million tons. Each ton of coke can produce about 350-450 cubic meters of coke oven gas. The hydrogen content in coke oven gas accounts for about 50-60%. It can produce by-product hydrogen. More than 7 million tons, a huge amount, accounting for 90% of the total amount of industrial by-product hydrogen. In addition to being used for combustion recovery, city gas, power generation and chemical production, the remaining part can be produced by pressure swing adsorption (PSA) purification technology to produce high-purity, low-cost hydrogen (purification and hydrogen operation cost 0.3-0.5 yuan/m³). Coke oven gas has complex components, low raw material gas pressure, and high product hydrogen purity requirements. The process flow consists of a compression process, a pretreatment process, a pressure swing adsorption process, and a purification process. In addition, in order to enable the sewage discharged by the system to meet the environmental protection requirements, it should also be equipped with a set of sewage treatment procedures. The key to hydrogen production from coke oven gas lies in the purification of impurities and the control of trace impurities in product hydrogen. Only by solving these two problems can we produce stable hydrogen for a long period of time and meet the requirements of hydrogen fuel cells.

3.2. Purification process of chlor-alkali by-product hydrogen

Considering that although the scale of coke oven gas hydrogen production is relatively large, the purity of the hydrogen produced is not high (sulfur-containing), and the hydrogen production process takes a long time and pollutes the environment. If the desulfurization and denitration steps are added, the hydrogen production is increased. Cost. In contrast, chlor-alkali by-product hydrogen production has the advantages of low purification cost, low difficulty, and high purity. Coal-to-hydrogen contains more impurities, which requires higher purification equipment and increases costs. Therefore, it is more common to use hydrogen as a by-product of the chlor-alkali industry to supply fuel cells as raw materials. The chlor-alkali plant uses salt water (NaCl) as raw material, uses ion membrane or asbestos diaphragm electrolyzer to produce caustic soda (NaOH) and chlorine gas (Cl₂), and at the same time can obtain by-product hydrogen. After removing impurities by the PSA hydrogen extraction device, high-purity hydrogen can be obtained (hydrogen purity can reach 99%-99.999%). At present, many chlor-alkali plants use part of the recovered hydrogen in hydrogen peroxide, pharmaceuticals, electronics and other industries. The production cost of 1 m³ of pure hydrogen is about 1.3 yuan.

My country is the country with the largest caustic soda production capacity in the world, accounting for 40% of global production capacity. In addition to the decline in output in 2015, it has maintained a relatively large growth momentum in recent years, with output basically stable between 30 million and 35 million tons. According to the chlor-alkali balance table, the output ratio of caustic soda to hydrogen is 40:1. It is calculated based on the production of 270m³ of hydrogen produced by producing 1t of caustic soda. my country’s chlor-alkali industry produces 750,000-875,000 tons of hydrogen by-product each year. At present, about 60% of the hydrogen in the chlor-alkali plant is used by supporting
polyvinyl chloride and hydrochloric acid, and the remaining about 280,000 to 340,000 tons are directly burned to generate heat energy. However, due to the large investment in the latter, up to 30% of the hydrogen is actually directly vented by the chlor-alkali plant. Calculated on the basis that each hydrogen fuel cell vehicle is filled with 5 kg of hydrogen per day, these remaining by-produced hydrogen can drive more than 150,000 fuel cell vehicles per year. A single enterprise of chlor-alkali chemical industry can make use of venting by-product hydrogen production is small, and the production capacity is scattered, the venting hydrogen volume available to a single enterprise does not exceed 10,000 tons. Therefore, the by-product hydrogen produced by the chlor-alkali industry is more suitable for transportation using gas hydrogen with a shorter transportation radius.

3.3. Light hydrocarbon cracking process
In addition to the above-mentioned two types of industrial by-product hydrogen, by-product hydrogen from light hydrocarbon cracking, including propane dehydrogenation (PDH) and ethane cracking, can also be used as a potential source of hydrogen for fuel cells. The raw material composition of the light hydrocarbon determines that its hydrogen impurity content is much lower than that of coal-to-hydrogen and coke-oven gas to produce hydrogen. Therefore, the purity of hydrogen is higher and purification is less difficult. ASIACHEM's consulting data shows that as of May 2018, there were 8 PDH projects in operation and 5 under construction in China. There are also a number of enterprise PDH projects in preliminary work, of which 4 have exact production year plans and 17 PDH The total propylene production capacity of the project will reach 9.75 million tons/year and the by-product hydrogen will be 370,000 tons/year. Based on the calculation of 5 kg of hydrogen per hydrogen fuel cell vehicle per day, these by-product hydrogen can provide about 200,000 hydrogen fuel cells per year Car driving.

4. Hydrogen production from water electrolysis
Electrolyzed water is an electrochemical process that splits water into hydrogen and oxygen. By this method, very high purity hydrogen can be produced. Depending on the type of technology and the load factor, the efficiency of the current electrolyzer system is between 60% and 81%. There are currently three main electrolysis cell technologies: alkaline electrolysis cell (AE), proton exchange membrane (PEM) electrolysis cell and solid oxide electrolysis cell (SOEC). The alkaline electrolyzer technology is the most mature and the production cost is low. The maximum gas production of a single domestic unit is 1000 cubic meters/hour; the proton exchange membrane electrolyzer has a simple process and high energy efficiency. The maximum gas production of a single domestic unit is 50 cubic meters/hour Because of the use of precious metal electrocatalysts and other materials, the cost is relatively high; the solid oxide water electrolysis cell adopts steam electrolysis, which has the highest energy efficiency and is still in the laboratory research and development stage. The advantages of hydrogen production from electrolyzed water are green environmental protection, flexible production, high purity (usually above 99.7%) and by-product high-value oxygen, etc. The purity of its hydrogen products can generally reach 99-99.9% level, and the main impurities are only H2O and O2 is especially suitable for proton exchange membrane fuel cells with strict requirements on the content of impurities such as CO. However, its unit energy consumption is about 4-5 kWh/cubic hydrogen, and the production cost is greatly affected by the electricity price, which accounts for more than 70% of the total cost. According to the China Hydrogen Energy Alliance, if the city power is used, the cost of hydrogen production is about 30-40 yuan/kg. It is generally believed that when the electricity price is lower than 0.3 yuan/kWh (utilizing the "valley electricity" electricity price), the cost of producing hydrogen from electrolyzed water will be close to that of traditional fossil energy.

China is rich in renewable energy and ranks first in the world in terms of development efforts. New energy and new installed capacity rank first in the world, but new energy power generation capacity fluctuates greatly due to seasonal and climate influences, and it cannot meet the stability of the load on the electricity side. The phenomenon of abandoning wind and light is very serious. A large amount of wind and water, and water and light is a favorable condition for the development of hydrogen production from electrolytic water. To produce low-cost hydrogen, sufficient low-cost power must be obtained to
ensure that the electrolyzer can run for a long time. A large number of low-cost power generation generated by the promotion of renewable energy, use it for water electrolysis to produce hydrogen and store it for later use. One of the methods. According to data from the China Hydrogen Energy Alliance, the amount of hydrogen produced by wind, light, water and nuclear hydrogen production in some areas is about 2.63 million tons per year.

Due to the instability of the voltage generated by the abandoned wind and abandoned electricity, it is difficult to promote on a large scale. The unsustainability of abandoned electricity limits its use, because electrolyzers that operate at high load and pay extra power cost more than those that only operate at low loads. Lower. If low-cost power can only be used for less time in a year, it means that the utilization rate of the electrolytic cell is low, and the high capital expenditure causes the cost of hydrogen to become higher. Although the cost of electricity increases with time, the improvement of the utilization rate of the electrolytic cell can Reduce the unit cost of hydrogen. Therefore, in the long run, abandoning electricity is not the best choice to solve the cost of hydrogen production from electrolyzed water. In the future, photovoltaic and wind power and other renewable energy parity grids provide another option for grid electricity generation. As the cost of solar power and wind power is reduced, the construction of hydrogen in electrolyzers in areas rich in renewable resources may become a low-cost source of hydrogen.

5. Conclusion
Hydrogen production is an important link in the economic consideration of hydrogen energy utilization. The development trend of hydrogen energy: combined with the actual conditions in various regions, there is no single optimal path. At present, China’s resources available for hydrogen supply of fuel cell vehicles are very considerable, and the alternative hydrogen production routes are also more diverse: in terms of renewable energy, only waste electricity can produce clean hydrogen if it is all used to electrolyze water to produce hydrogen. 200 10,000 tons or more; in terms of industrial by-product hydrogen production, the chlor-alkali industry, together with propane dehydrogenation and the upcoming ethane cracking project, can produce a total of more than 1 million tons of by-product hydrogen; the two can provide more than 3 million tons of clean hydrogen, Enough to meet the needs of the hydrogen energy industry in the short and medium term

However, the economics of various types of hydrogen production routes are not enough to ensure the large-scale commercialization of fuel cell vehicles. Reference the average raw material price to compare the cost of hydrogen production under different hydrogen production processes: the cost of hydrogen production from coal is 9-11 yuan/kg, which is currently the lowest cost hydrogen production route in China (coal price is 550 yuan/ton); natural gas hydrogen production The cost is 20-24 yuan (natural gas price is 3.5 yuan/cubic meter); methanol hydrogen production cost is 23 yuan-25 yuan/kg (methanol price is 3000 yuan/ton); electrolytic water hydrogen production cost is 40 yuan-50 yuan/kg (when the price of electricity is 0.6 yuan/kWh). The average cost of industrial by-product hydrogen is 12 yuan-18 yuan/kg.

The price of raw materials and the price of local basic energy determine the production cost of hydrogen produced by fossil energy and electrolyzed water; capital expenditures such as purification treatment equipment determine the cost of industrial by-product hydrogen. At the same time, it should also be considered that the current hydrogen storage and transportation links are constrained. The hydrogen transportation bottleneck has not yet been completely broken through and the cost is higher. Sometimes the storage and transportation costs that downstream users need to pay are even higher than the hydrogen production costs. At present, hydrogen transportation is mainly based on short-distance gas transportation of tube trailers, and the economic radius is within 200-300km; liquid hydrogen transportation and pipeline transportation have not yet been applied on a large scale, long-distance hydrogen transportation costs are high, and the infrastructure of the entire hydrogen supply system is not yet sound. Taking a hydrogen refueling station in Shanghai as an example, the ex-factory price of the chlor-alkali hydrogen produced by the purchase is 20 yuan/kg, and the arrival price after storage and transportation has exceeded 50 yuan/kg. It can be seen that under the current hydrogen supply system,
the cost of hydrogen including production, storage and transportation is not competitive in the market. Therefore, it is more reasonable to choose a hydrogen source with suitable production cost according to the regional resource endowment and the downstream hydrogen consumption market is within the transportation economic radius.

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