Analysis on the Methods of Hydrogen Generation

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Abstract. The purpose of this paper is to analyze the methods of hydrogen generation. More specifically, it explains methods of several hydrogen generation, studies their existing advantages and challenges, and finally draws a conclusion of comparative advantages through analysis and comparison. In order to support this analysis, specific methods of the four categories of hydrogen generation methods proposed by the United States Department of Energy are investigated, and the essential concerns and ideas from various papers and websites were referenced and integrated to find out the advantages and disadvantages of specific hydrogen generation processes. According to the idea of sustainable development, as well as the use of hydrogen energy for clean energy replacement and renewable energy storage, it is finally considered that Solid oxide electrolytic cell (SOEC) generation hydrogen generation process is relatively the most suitable for the use of hydrogen, sustainable, and has broad future prospects. This paper can provide a detailed description of hydrogen generation and propose the future development direction of hydrogen generation.

Keywords: hydrogen generation, thermochemical processes, direct solar water splitting processes, biological processes, electrolytic processes.

1. Introduction

In an era defined by a growing global concern for environmental degradation and a looming energy crisis, the search for sustainable and eco-friendly energy sources has never been more critical. The realization that traditional fossil fuels are both finite and responsible for a substantial portion of greenhouse gas emissions has compelled humanity to seek alternative solutions to power our modern world. One such solution, gaining increasing attention and momentum, is the utilization of hydrogen as an energy source. Hydrogen, as an energy carrier, offers versatility, high energy density, and the benefits of conserving renewable energy through electrical conversion. Most importantly, its emission-free combustion reduces carbon emissions and mitigates the impact on the climate.

However, hydrogen's share in the global energy mix is relatively low. Traditionally, fossil fuels such as oil, natural gas, and coal have dominated. Nevertheless, due to growing attention towards renewable and clean energy sources, hydrogen's potential as a clean energy carrier has garnered widespread interest and has been actively promoted in some countries and regions.

Currently, hydrogen can be produced through various methods, with four primary approaches being through thermochemical processes, direct solar water splitting processes, biological processes, and electrolytic processes. Analyzing and comparing these methods is crucial in determining the preferred approach [1].

2. Methods of Hydrogen Generation

2.1. Thermochemical Processes

2.1.1. Natural Gas Reforming

Natural gas contains methane (CH_4) which can undergo thermochemical reactions such as steam-methane reforming reaction, where methane, water, and heat will react to form carbon monoxide and hydrogen, or partial oxidation, where methane reacts with oxygen to form carbon dioxide, hydrogen and heat, of methane reaction to produce hydrogen.

2.1.2. Biomass Gasification

In the process of biomass gasification, biomass (including hydrocarbon and oxygen) is converted to carbon monoxide, carbon dioxide, and hydrogen at temperatures greater than 700 degrees Celsius without combustion and in reaction with oxygen. The carbon monoxide also forms hydrogen through a water-gas shift reaction. Finally, in order to separate and extract hydrogen, adsorbents or particular membranes are used.

2.1.3. Biomass-derived Liquid Reforming

In the first step, cellulosic ethanol, bio-oils, or other liquid biofuels react with steam under the conditions of catalyst and high temperature to form a mixture of gases, mainly hydrogen, carbon monoxide, and carbon dioxide. And then the water-gas shift reaction will follow. Eventually, produced hydrogen will be extracted.

2.1.4. Thermochemical Water Splitting

The process uses water at temperatures between 500 and 2,000 degrees Celsius to drive a series of chemical reactions to produce hydrogen. It is worth mentioning that the chemicals used can be reused to create a closed loop that uses only water to produce hydrogen and oxygen. The heat required is generated in two ways: by using "heliostats" mirrors that focus sunlight on the reactor; or using waste heat from advanced nuclear reactors.

2.2. Direct Solar Water Splitting Processes

2.2.1. Photoelectrochemical (PEC)

PEC water solution method will soak a semiconductor material, which is similar to that used in photovoltaic solar power generation materials, in water-based electrolyte, which can directly convert solar energy into semiconductor energy to intensify the decomposition of water.

2.2.2. Photobiological

In photolysis biological systems, microorganisms such as green algae or cyanobacteria use solar energy to split water into oxygen anions and hydrocation ions, which can be converted directly or indirectly into hydrogen.

2.3. Biological Processes

2.3.1. Microbial biomass conversion

In some bio-decomposition processes, microorganisms can break down complex organic matter directly into a mixture containing hydrogen through different means. Hydrogen can be separated and extracted directly from it.

2.3.2. Photobiological

It was mentioned in the Direct Solar Water Splitting Process above. It will not be explained again here.

2.4. Electrolytic Processes

2.4.1. Alkaline Water Electrolytic Cell

Alkaline electrolytic water technology is based on KOH, NaOH aqueous solution as electrolyte, such as the use of asbestos cloth as a diaphragm, under the action of direct current, the water is electrolyzed into hydrogen and oxygen.

At the cathode, water molecules are split into hydrogen ions and hydroxide ions, which give electrons to hydrogen atoms and further form hydrogen molecules.

The hydroxide ions pass through the porous diaphragm under the electric field force between the negative and the anode and reach the anode, where they lose electrons to form water and oxygen molecules.

2.4.2. Solid Oxide Electrolytic Cell (SOEC)

The working mechanism of SOEC can be seen in fig.1. When a certain voltage is applied outside the electrolytic cell, under the action of electromotive force, H_2O at the hydrogen electrode is decomposed into H_2 and O^{2-} under the catalysis of Ni.

$$H_2O + 2e^- \rightarrow H_2 + O^{2-} \quad (1)$$

The resulting O^{2-} passes through the electrolyte layer to the oxygen electrode and loses electrons to form O_2 under the action of the catalyst.

$$O^{2-} \rightarrow 2e^- + 1/2O_2 \quad (2)$$

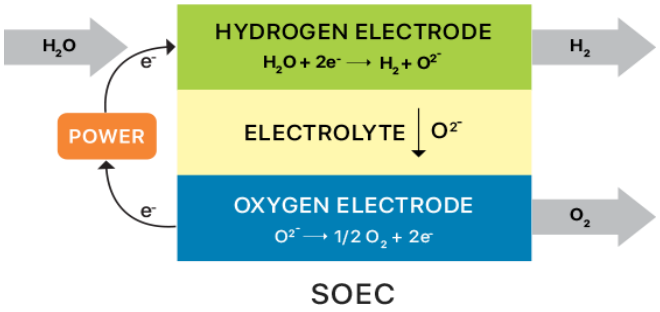


Figure 1. H2 production by steam electrolysis in SOEC mode [2]

2.4.3. PEM Pure Water Electrolytic Cell

PEM electrolysis water hydrogen production technology uses a proton exchange membrane as a solid electrolyte instead of the diaphragm and liquid electrolyte used in alkaline electrolytic cells (30% potassium hydroxide solution or 26% sodium hydroxide solution), and uses pure water as the raw material for electrolysis water hydrogen production, avoiding potential lye contamination and corrosion problems [3].

3. Advantages and Challenges of Major Division of Process

3.1. Thermochemical Processes

3.1.1. Natural Gas Reforming

Advantages: Low-cost Natural gas reform can provide hydrogen for many applications such as fuel cell electric vehicles (FCEVs). In addition, during the entire process of producing, transporting and storing hydrogen, the greenhouse gas emissions of FCEVs are reduced by half compared to today's petroleum vehicles.

Challenges: Potential production of more carbon-containing substances. External heat transfer devices are required, which leads to system complexity and potentially higher costs. An external igniter is required to initiate the reaction, resulting in a larger volume and slower start [4, 5].

3.1.2. Biomass Gasification

Advantages: Biomass is a kind of renewable organic resources, such as crop residues, forest residues, etc. They are an abundant resource in most countries. In the United States, for example, 1 billion tons of biomass (without water) can be used as energy every year. Biomass is mainly produced by plants through photosynthesis, and in this process, plants will consume carbon dioxide in the atmosphere, which can offset the carbon dioxide released by biomass gasification to produce hydrogen, reducing net greenhouse gas emissions.

Challenges: Pretreatment of biological feedstock: Municipal solid waste classification; Pulverizing the biological raw materials. Biogenic Feedstocks Feeding: Feedstock low density issues; Connection and clogging of raw material transfer pipeline. Biogenic Feedstocks Gasification: Lacking of kinetic

and mineral data; Tar Formation and In-situ Cracking; Control and operation of gasifiers; Alternative Oxygen Supply Methods; Syngas Cleanup and Heat Recovery: Detarring system; Heat recovery challenge [6].

3.1.3. Biomass-derived Liquid Reforming

Advantages: This method does not solely have the advantages mentioned above: the source of raw materials is wide and abundant, and the net carbon emission is low; There is also the benefit of being a better liquid which would be easy to transport.

Challenges: Similar to the problems with biomass gasification, biomass-derived liquids are prohibitively expensive to install, operate and maintain. And the efficiency of the whole process is also relatively low [7].

3.1.4. Thermochemical Water Splitting

Advantages: The entire high-temperature thermochemical water decomposition process is powered by clean solar and nuclear energy, and the raw material is only water, with virtually no greenhouse gas emissions.

Challenges: The efficiency and sustainability of materials involved in thermochemical cycles needs to be improved. The efficiency and robustness of the reactor needs to be improved to be compatible with higher temperatures. The cycle of heat needs to continue to develop. For solar thermochemical systems, the cost of condenser systems is too high [8].

3.2. Direct Solar Water Splitting Processes

3.2.1. Photoelectrochemical (PEC)

Advantages: The use of solar and nuclear power makes the process clean and scalable. Using only water as the raw material, this method causes almost no greenhouse gas emissions.

Challenges: Low efficiency, need to improve the absorption of sunlight and surface catalysis. Durability and service life are lower, requiring stronger materials and protective surface coatings. The cost of materials and materials processing is high [9].

3.2.2. Photobiological

Advantages: Photobiological production technology is clean and low cost. This technology has low or even zero carbon emissions. It can also treat water that cannot be used for drinking or agriculture, and even waste water.

Challenges: Due to the size and scale of the microorganisms, the efficiency of hydrogen generation is low. Need to discover new enzymes and improve enzyme activity; Or develop more advanced microbes. Oxygen as a product inhibits the forward reaction rate, and mixing oxygen with hydrogen creates safety concerns [10].

3.3. Biological Processes

Advantages: Biomass resources and raw materials are very rich. The quantity of microbes that can break down biomass are huge. MEC's system can produce hydrogen from resources and wastewater that cannot be used for fuel production, while saving energy and resources for treating waste and wastewater.

Challenges: The rate and yield of fermentation process are very low. It is necessary to improve the strain of microorganisms, optimize the reactor system, and improve the efficiency of the enzymatic reaction. MEC systems cannot be commercialized and scaled in maintaining laboratory-scale productivity and system efficiency. The cost of the reactor components is too high [11].

3.4. Electrolytic Processes

3.4.1. Alkaline Water Electrolytic Cell

Advantages: Alkaline electrolysis is a clean and sustainable method of producing hydrogen because it can be powered by renewable energy sources such as wind and solar power. The technology

in Alkaline electrolysis is relatively mature, so its scale and size can be adjusted according to the entire hydrogen production facility.

Challenges: The energy efficiency of alkaline electrolyzer is low, usually about 60%. Alkaline electrolytes (such as KOH) will react with CO_2 in the air to form water-insoluble carbonates under alkaline conditions, which will block the porous catalytic layer, hinder the transfer of products and reactants, and greatly reduce the performance of the electrolyzer. The alkaline electrolytic cell is difficult to quickly close or start, and the hydrogen production speed is difficult to adjust quickly, because the pressure on both sides of the anode and cathode of the electrolytic cell must be kept balanced at all times to prevent hydrogen and oxygen gas from mixing through the porous asbestos film and causing an explosion.

3.4.2. PEM pure water electrolytic cell

Advantages: PEM electrolysis water hydrogen production technology has the advantages of high current density, high hydrogen purity, and fast response speed. The current density of PEM electrolyzers is higher, usually above 10000 A/m2. The purity of hydrogen produced by PEM electrolyzers is usually around 99.99%. Since the PEM electrolytic cell uses pure water as the electrolytic raw material, the hydrogen generated will not be brought into the alkali fog, which is conducive to improving the quality of hydrogen. In addition, the proton exchange membrane has a low gas permeability, which helps to avoid the phenomenon of gas cross penetration of hydrogen and oxygen. PEM electrolyzers do not need to strictly control the pressure on both sides of the membrane, and have the advantages of fast start and stop and fast power regulation response, which is suitable for renewable energy generation volatility input.

Disadvantages: The current equipment cost of PEM electrolysis water hydrogen production technology is high, and the unit cost of PEM electrolyzer is still much higher than that of alkaline electrolyzer. Because PEM electrolyzers need to operate in a highly acidic and highly oxidizing working environment, the equipment is more dependent on expensive precious metals such as iridium, platinum, and titanium, resulting in high costs.

3.4.3 Solid Oxide Electrolytic Cell

Advantages: SOEC operates at a high temperature of 700-850 degrees, which can speed up the rate of electrode reaction, significantly reduce the overpotential of the cathode and anode, effectively reduce the energy loss of the electrolytic process, and the system efficiency can reach 85%. The principle of SOEC is to decompose water molecules, after the evaluation and comparison of the United States Department of Energy, electrical energy consumption is low energy consumption. SOEC is a reversible fuel cell used for the storage of renewable energy. Form the mutual conversion of electricity and hydrogen. Its cycle efficiency and reversibility are estimated to reach 52% and 30% in 2024. The primary reactant of SOEC is water vapor. When carbon dioxide is added, syngas, a mixture of hydrogen and carbon monoxide, is produced. Further production of synthetic fuels, such as diesel and jet fuel. So SOEC technology can contribute to carbon dioxide recovery and fuel production.

Challenges: The development of SOEC started late, the scale is small, and the development process is slow. The industrial chain of SOEC is not perfect. The supply chain is incomplete. For example, companies find it difficult to find manufacturers when they are short of parts. There are technical difficulties with SOEC. The operating temperature of SOEC is high, which requires high temperature resistance and corrosion resistance of materials.

4. Conclusion

According to analysis, the advantages of Electrolytic Processes compared to the other four hydrogen production processes exists. Electrolytic processes offer cleanliness and sustainability as they can utilize renewable energy sources such as wind and solar power to generate hydrogen. This contributes to reducing greenhouse gas emissions, aligning with sustainable development goals. In

contrast, processes like natural gas reforming and biomass gasification may rely on fossil fuels, leading to higher carbon emissions. Particularly, Proton Exchange Membrane (PEM) electrolysis and Solid Oxide Electrolysis Cell (SOEC) electrolysis provide exceptionally high hydrogen purity, typically reaching around 99.99%. This is crucial for many applications, especially fuel cells. Natural gas reforming and biomass gasification processes may produce impurities, resulting in less pure hydrogen. PEM and SOEC electrolysis processes exhibit the capability for rapid start-stop and quick power adjustment responses. This allows them to better accommodate fluctuations in renewable energy input. In contrast, other processes may require more time to initiate or halt, leading to slower response times. SOEC electrolysis processes boast high energy efficiency, with system efficiency reaching up to 85%. Moreover, they function as reversible fuel cells, converting electrical energy into hydrogen and enabling energy storage. Anticipated improvements in cycle efficiency and reversibility further enhance their appeal. In contrast, natural gas reforming and biomass gasification processes may exhibit lower energy efficiency. SOEC electrolysis processes can produce synthesis gas, which can be further utilized in the production of synthetic fuels such as diesel and jet fuel. This contributes to reducing carbon emissions and supporting sustainable fuel production—an aspect not readily available in other processes. In summary, electrolytic processes, particularly SOEC electrolysis, exhibit distinct advantages in terms of cleanliness, hydrogen purity, responsiveness, energy efficiency, and potential for synthetic fuel production when compared to other hydrogen production processes. These characteristics make them better suited for achieving sustainable hydrogen production to meet future energy demands.

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