Analysis of several main hydrogen production technologies

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Abstract. With economic development, social progress, and population growth, mankind’s demand for energy increases. Fossil fuels such as coal, oil, and natural gas are accelerating consumption, and these fossil fuels are non-renewable, and their reserves are very limited. If we continue to use fossil fuels uncontrollably, it will inevitably cause acid rain and global warming. As a renewable energy source, hydrogen energy has the least environmental pollution, and hydrogen energy can be dispersed in large quantities and converted from renewable energy. At present, hydrogen production technology and cost are high. This article briefly explains the principles and advantages, and disadvantages of several hydrogen production technologies, etc., and the cost and work efficiency of various technologies. Studies have shown that biomass pyrolysis and photocatalytic hydrogen production have higher efficiency and lower cost, which can be used as future research directions. However, there are problems such as the unclear hydrogen production mechanism of biological pyrolysis and unstable solar energy. And its future research and development directions are discussed in more detail. The research on hydrogen production technology is to satisfy the requirements of national economic development and social development needs.

1. Introduction

Regarding the country’s economic development needs, as the constant changes in the international situation affect energy prices, the trend of rising fossil fuel prices is unstoppable, and people must try to prevent the energy crisis from happening. The gap between China's future energy supply and demand will become larger and larger. In the face of rising oil prices worldwide, the security of my country's energy supply will inevitably be threatened. In terms of social development needs, energy consumption worldwide is increasing, most of which use fossil fuels. Hydrogen energy, as a renewable energy source, has an impact on the environment. The least impact can be established based on clean energy centered on hydrogen energy. In terms of the needs of the development of science and technology, the development and utilization of hydrogen energy must first solve the problem of hydrogen energy. The production of a large amount of cheap hydrogen is the basis for realizing hydrogen energy utilization. Hydrogen is a high-density energy source. Generally speaking, the production of hydrogen requires to consume a lot of energy. Therefore, it is necessary to find a low-energy, high-efficiency hydrogen production method, especially a way to convert a large amount of dispersed renewable energy into hydrogen energy.

Someone has written a similar review before and has also researched hydrogen production technology and methods. The difference from the previous review is that this article briefly describes the principles and advantages, and disadvantages of several hydrogen production technologies, etc., and the cost and work efficiency of various technologies and their future research and development directions. This article is a more detailed discussion.
This article combines the literature reviewed on the Internet, compares various mainstream hydrogen production technologies, and selects hydrogen production technologies that need to be developed vigorously in the future from the perspective of cost and efficiency.

2. Hydrogen production from fossil fuels

\[ \begin{align*}
C + H_2O &\rightarrow CO + H_2 \quad \Delta H^{298K} = +144.0 \text{kJ/mol} \\
2C + O_2(N_2) &\rightarrow 2CO + (N_2) \quad \Delta H^{298K} = -195.5 \text{kJ/mol} \\
CO + H_2O &\rightarrow CO_2 + H_2 \quad \Delta H^{298K} = -41.2 \text{kJ/mol}
\end{align*} \]

2.1 Coal to hydrogen

2.1.1 Coal gasification hydrogen production

Under normal circumstances, coal gasification requires oxygen, so hydrogen production from coal also requires an air separation system. Hydrogen production by coal gasification is to first gasify coal to obtain gaseous products with H and CO as the main components and then undergo CO conversion, separation, and purification to obtain product hydrogen with a certain purity.

There is currently a plasma coal gasification process that can be applied to produce syngas from coal. In this process, shown in Figure 2, the raw materials in the system are decomposed. [1].

![Figure 1. Coal gasification hydrogen production process](image1)

![Figure 2. Plasma gasification hydrogen production process](image2)
2.1.2 Coal coking hydrogen production
The H₂ production from coke oven gas usually adopts an adsorption separation process [2]. Due to the high boiling point of C₅-6 saturated hydrocarbons, naphthalene, inorganic sulfur, tar, etc., it is difficult to desorb at room temperature after being adsorbed on the adsorbent. Therefore, the coke oven gas hydrogen production process usually uses two different adsorption devices: variable temperature Adsorption device; pressure swing adsorption device. After entering the station, the coke oven gas is first compressed into the temperature swing adsorption device to remove hydrocarbons above C₅ and gas high-boiling impurities to achieve the purpose of pre-purification of coke oven gas. Then pass through the pressure swing adsorption device to remove all impurities except O₂ and finally remove O₂ through catalytic reaction and dry to obtain H₂ with a volume percentage of H₂ greater than or equal to 99.999%. The entire coke oven gas hydrogen production process can be divided into four sections: compression and pre-purification, pre-treatment, pressure swing adsorption, and refining (figure 3.).

![Figure 3. The scheme of the COGH process [2]](image)

COGH now has a high degree of feasibility in hydrogen production [2]. The use of clean coal gasification technology can produce clean energy. Although the use of coal to produce hydrogen was commercially successful at the time, these basic problems have been overcome today in areas where there are no alternative raw materials in the world, such as in China [3].

2.2 Hydrogen production from natural gas
The emissions of a typical SMR plant are around 9–11 kg CO₂ per kg H₂ [4], [5]. Based on the 2016 hydrogen production capacity of U.S. refineries of 9300 tonne/day [6], [7].

\[
\begin{align*}
C_nH_m + xH_2O &\rightarrow xCO + (x+y/2)H_2 \quad (4) \\
CO + H_2O &\rightarrow CO_2 + H_2 \quad (5) \\
CH_4 + CO_2 &\rightarrow 2CO + 2H_2 \quad (6)
\end{align*}
\]

2.3 Hydrogen production from heavy oil
The partial oxidation process of heavy oil includes pressurization, preheating and mixing of raw oil and gasification agent, high-temperature non-catalytic partial oxidation reaction, high-temperature synthesis gas waste heat recovery, gas product washing, and carbon black removal, carbon black recovery, and sewage treatment. The process is carried out under a certain pressure, and catalysts can be used or not, depending on the selected raw materials and processes. Catalytic partial oxidation usually uses methane or naphtha-based low-carbon hydrocarbons as raw materials, while non-catalytic partial oxidation uses...
heavy oil as raw materials. The reaction temperature is between 1150 and 1315°C. Compared with methane, heavy oil has higher hydrocarbons [8]. The principle of a typical partial oxidation reaction is as follows:

\[ C_nH_m + n/2O_2 = nCO + m/2H_2 \]  \hspace{1cm} (7)

\[ C_nH_m + nO_2 = nCO + (n + m/2)H_2 \]  \hspace{1cm} (8)

\[ H_2O + CO = H_2 + CO_2 \]  \hspace{1cm} (9)

It has certain cost advantages for hydrogen production. In addition, the partial oxidation of heavy oil is an exothermic reaction, and the reaction between heavy oil and steam is an endothermic reaction. When the endothermic heat of the reaction is greater than the exothermic heat, additional heavy oil can be burned to balance the heat. Compared with hydrogen production by steam reforming of natural gas, the operating temperature and pressure of hydrogen production by partial oxidation of heavy oil are higher, and it is easier to reach equilibrium. The disadvantage is that the cost of equipment investment for hydrogen production by partial oxidation of heavy oil accounts for a large proportion of the cost. Rising international oil prices also increase the cost of raw materials. In addition, a certain amount of sulfide gas will be produced after the heavy oil is partially oxidized, which will inevitably cause a certain impact on the environment.

3. Hydrogen production from biomass

3.1 Thermochemical productions

Thermochemical conversion is the most advanced technology for hydrogen production from biomass [9]. The process is based on a similar methodology for biofuels (such as biomethane) [10], adapted from Steam Methane Reforming (SMR) [11], [12].

The general steam gasification reaction of biomass is presented in Equation (10).

\[ \text{Biomass} + \text{Steam} \rightarrow \text{H}_2 + \text{CO} + \text{CO}_2 + \text{CH}_4 + \text{HC} + \text{Tar} + \text{Char} (\Delta H^o > 0 \text{kJ/mol}) \]  \hspace{1cm} (10)

| Products | Air gasification | Oxygen gasification | Steam gasification |
|----------|------------------|---------------------|--------------------|
| \( \text{N}_2, \text{CO}, \text{H}_2, \text{CO}_2, \text{LHC(CH}_4\text{C}_3\text{H}_4),\text{H}_2\text{O} \) | \( \text{CO}, \text{H}_2 \) | \( \text{CO}_2, \text{LHC(CH}_4\text{C}_3\text{H}_4),\text{CO}_2 \) |
| Average \( \text{H}_2 \) composition | 15% | 40% | 40% |
| \( \text{H}_2/\text{CO} \) ratio | 0.75 | 1 | 1.6 |
| Heating Value (MJ/Nm\(^3\)) | 4 to 7 | 12 to 28 | 10 to 18 |

Biomass+Heat\( \rightarrow \text{H}_2 + \text{CO} + \text{CO}_2 + \text{CH}_4 + \text{H}_2\text{O} + \text{bio-oil} + \text{charcoal} (\Delta H^o > 0 \text{kJ/mol}) \)  \hspace{1cm} (11)

The separation of the reactor in the pyrolysis-steam reforming process avoids the inhibition of the reforming catalyst by coke deposition [13].
3.2 Biological conversion

These microorganisms can produce $\text{H}_2$ (together with $\text{CO}_2$) in the dark by oxidising $\text{CO}$ and reducing $\text{H}_2\text{O}$ through an enzymatic pathway, according to Equation (12) [14], [15]:

$$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 (\Delta H^\circ > 0 \text{kJ/mol})$$

Equation (13) presents the global reaction performed on glucose as the model substrate [16]:

$$\text{C}_6\text{H}_{12}\text{O}_6 + 12\text{H}_2\text{O} \rightarrow 12\text{H}_2 + 6\text{CO}_2$$

3.3 Electrochemical conversion

Biomass-derived has low hydrogen purity. There are also issues such as photosynthetic efficiency, water and soil area, concentration, and storage costs [11]. Compared with biochemical processes, thermochemical processes require less time. However, thermochemical processes require higher energy input and continuous removal of tar from the product. In addition, compared with biochemical processes, thermochemical processes have higher efficiency and lower costs. However, this method produces very little hydrogen and has not been commercialized. Gasification is considered to be one of the most effective methods for producing hydrogen from biomass. The challenge of gasification is low efficiency. The biochemical process is in line with converting organic materials by microorganisms into a mixture of various compounds, including hydrogen [17].

4. Hydrogen production by water splitting

4.1 Electrochemical hydrogen production

Water splitting could release $\text{H}_2$ and $\text{O}_2$ by adding electricity, as described in Eq (14).

$$\text{H}_2\text{O} \rightarrow 1/2\text{O}_2 + \text{H}_2$$

However, the production cost of hydrogen production by electrolysis of water is relatively high. At present, the output of hydrogen production by electrolysis of water only accounts for 1% to 4% of the
total output. However, electrolyzed water has the characteristics of high product purity and relatively simple operation, and its production history is very long. This method can directly produce a purity of 99 degrees. More than 7% of hydrogen, simple operation, small impact on the environment, but high-power consumption, so the application is subject to certain restrictions. With the gradual expansion of the application of hydrogen energy, the method of producing hydrogen by electrolysis of water will surely be developed. In the electrolysis water reaction, Pt is the best catalytic material for catalyzing the semi-reaction of hydrogen evolution. Compared with the hydrogen evolution reaction, the oxygen evolution half-reaction is more difficult in terms of kinetics, resulting in low energy conversion efficiency of the entire water-splitting system. Currently, commercial oxygen evolution catalyst materials are mainly noble metal oxides such as Ir O₂ and RuO₂. However, the scarcity and high cost of the above-mentioned noble metal-based catalytic materials severely limit their wide application. Therefore, it has important scientific and engineering significance to reduce the number of precious metals and improve the activity of precious metal catalytic materials, especially to find a new high-efficiency metal catalytic material system with abundant reserves and low prices that can replace them precious metals.

4.2 Photocatalytic hydrogen production

The basic process of the semiconductor photocatalytic hydrogen production reaction (figure 6): the semiconductor absorbs photons with energy equal to or greater than the band gap (Eg), and the electron transitions from the valence band to the band. This light absorption is called intrinsic absorption and the photocatalytic oxidation reaction requires the valence band potential to be greater than the donor's E(D/D⁻) is positive; in other words, the energy level at the bottom of the conduction band is higher than the E (D/D⁻) energy level of the acceptor, and the energy level at the top of the valence band is lower than the E (D/D⁻) energy level of the donor.

5. Hydrogen production cost

From the table, we can see that the cost of biomass pyrolysis, solar photovoltaic power generation, and solar thermal decomposition is the lowest. It is possible to achieve high-efficiency and low-cost requirements for hydrogen production in the future.

| Process                          | Energy source | Feedstock | Capital cost(M$) | Hydrogen cost($/kg) |
|----------------------------------|---------------|-----------|------------------|---------------------|
| Steam methane reforming          | Fossil fuels  | Natural gas| 180.7 to 226.4   | 2.08 to 2.27       |
| Goal gasification                | Fossil fuels  | Coal      | 435.9 to 545.6   | 1.34 to 1.63       |
| Autothermal reforming of methane | Fossil fuels  | Natural gas| 183.8            | 1.48                |
### Methane pyrolysis
- **Generated steam:** Internally generated
- **Feedstock:** Natural gas
- **H\(_2\) yield:** 1.59 to 1.70

### Biomass gasification
- **Generated steam:** Internally generated
- **Feedstock:** Woody biomass
- **H\(_2\) yield:** 3.1 to 53.4
- **Cost:** 1.25 to 2.20

### Biomass pyrolysis
- **Generated steam:** Internally generated
- **Feedstock:** Woody biomass
- **H\(_2\) yield:** 6.4 to 149.3
- **Cost:** 1.77 to 2.05

### Direct bio-photolysis
- **Power source:** Solar
- **Feedstock:** Water+algae
- **Cost:** 50$/\text{m}^3$
- **H\(_2\) yield:** 2.13

### Indirect bio-photolysis
- **Power source:** Solar
- **Feedstock:** Water+algae
- **Cost:** 135$/\text{m}^3$
- **H\(_2\) yield:** 1.42

### Dark fermentation
- **Feedstock:** Organic biomass
- **H\(_2\) yield:** 2.57

### Photo fermentation
- **Feedstock:** Organic biomass
- **H\(_2\) yield:** 2.83

### Solar photovoltaic electrolysis
- **Power source:** Solar
- **Feedstock:** Water
- **H\(_2\) yield:** 12.0 to 54.5
- **Cost:** 5.78 to 23.27

### Solar thermal electrolysis
- **Power source:** Solar
- **Feedstock:** Water
- **H\(_2\) yield:** 22.1 to 421.0
- **Cost:** 5.10 to 10.49

### Wind electrolysis
- **Power source:** Wind
- **Feedstock:** Water
- **H\(_2\) yield:** 499.6 to 504.8
- **Cost:** 5.89 to 6.03

### Nuclear electrolysis
- **Power source:** Nuclear
- **Feedstock:** Water
- **H\(_2\) yield:** 39.6 to 2107.6
- **Cost:** 2.17 to 2.63

### Nuclear thermolysis
- **Power source:** Nuclear
- **Feedstock:** Water
- **H\(_2\) yield:** 5.7 to 16.0
- **Cost:** 7.89 to 8.40

### Photoelectrolysis
- **Power source:** Solar
- **Feedstock:** Water
- **H\(_2\) yield:** 10.36

### Conclusion
As the hydrogen production technology becomes more and more mature now, the current hydrogen production technologies include coal gasification, hydrogen production from coal coking, hydrogen production from heavy oil, hydrogen production from biomass, and hydrogen production from water splitting. Because the raw material for hydrogen production from coal is coal, a non-renewable energy source, so its application prospects are limited. Although the technology is relatively mature, it will still cause damage to the environment. Hydrogen production from biomass can increase production, help improve economic capacity, increase source flexibility, and reduce greenhouse gas emissions. Although there is no pollution to H\(_2\) generation from electrolyzed water, the production cost is relatively high. Most of them have low solar energy utilization and low recombination rate of photo-generated electron-hole pairs. In addition, another important restriction of photocorrosion or cycle stability must be resolved before practical application. These limitations bring about unsatisfactory hydrogen production efficiency and cruelly limit the practical application of photocatalysts.

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