STEAM REFORMING

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INTRODUCTION

In the existing energy supply system, electricity, gasoline, diesel fuel, and natural gas serve as energy carriers. These energy carriers are made by the conversion of primary energy sources, such as nuclear fission, fossil fuels as coal, petroleum, and natural gas into an energy form that is easily transported and delivered in a usable form to industrial, commercial, residential, and transportation end-users.

A sustainable future energy supply system would use electricity and hydrogen as the dominant energy carriers. Hydrogen would be produced from a diverse base of primary energy feed-stocks such as nuclear fission, wind energy and solar power using the resources and processes that are most economical or consciously preferred.

Methods to produce hydrogen from natural gas are well developed and account for over 95 percent of all hydrogen produced in the USA and 48 percent globally.

Figure 1. Steam methane reformer, Texas City, Texas. Source: Linde.

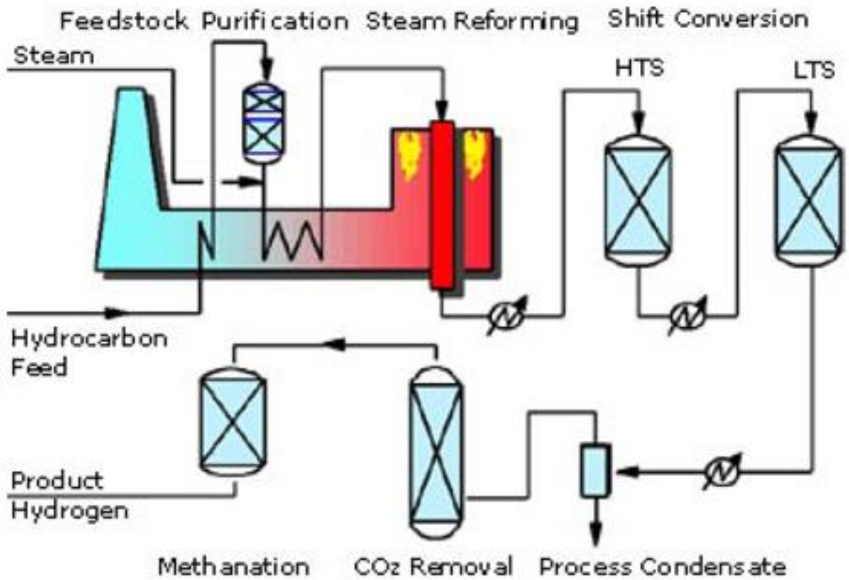

Figure 2. Steam reforming for hydrogen production.

STEAM METHANE REFORMING, SMR

The steam methane reforming (SMR) process is the most widespread method to generate hydrogen-rich synthesis gas from light carbohydrates.

The feed material can be natural gas, liquid gas or naphta. They are converted endothermically with steam into synthesis gas in catalytic tube reactors. Process heat as well as flue gases are used for the generation of steam.

It consists of two steps:

1. **Reformation process**

The first step of the SMR process involves a light hydrocarbon reacting with steam at 750-800°C or 1380-1470ºF to produce a synthesis gas or syngas, which is a mixture primarily made up of hydrogen, H_2 and carbon monoxide, CO.

The desulfurized hydrocarbon feed is mixed with superheated process steam in accordance with the steam/carbon relationship necessary for the reforming process. This gas mixture is heated up and then distributed on the catalyst-filled reformer tubes. The gas mixture flows from top to bottom through tubes arranged in vertical rows. While flowing through the tubes heated from the outside, the hydrocarbon/steam mixture reacts, forming hydrogen and carbon monoxide according to:

$$C_nH_m + nH_2O \rightarrow nCO + \frac{(2n+m)}{2}H_2 \qquad (1)$$

2. Shift Reaction

The second step, known as a Water Gas Shift (WGS) reaction, the CO produced in the first reaction is reacted with steam over a catalyst to form H2 and CO_2.

This process occurs in two stages, consisting of a High Temperature Shift (HTS) at 350 ºC or 662 ºF endothermic reaction:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \qquad (2)$$

and a Low Temperature Shift (LTS) at 190-210 ºC or 374-410 ºF exothermic reaction:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (3)$$

To minimize the CH_4 content in the synthesis gas while simultaneously maximizing the H_2 yield and preventing the formation of elemental carbon and keeping it from getting deposited on the catalyst, the reformer is operated with a higher steam/carbon relationship than theoretically necessary.

As the process is endothermic, the required heat must be produced by external firing. The burners for the firing are arranged on the ceiling of the firing area between the tube rows and fire vertically downward.

The residual gas from the pressure swing adsorption unit as well as heating gas from battery limits is used as fuel gas. The flue gas is then cooled down in a convection zone, generating steam.

PURIFICATION PROCESS

High to ultra-high purity hydrogen is needed for the durable and efficient operation of fuel cells.

Impurities are believed to cause various problems in the current state-of-the-art fuel cell designs, including catalyst poisoning and membrane failure. Additional process steps may be required to purify the hydrogen to meet industry quality standards.

Additional steps could also be needed if carbon capture and sequestration technologies are developed and utilized as part of this method of hydrogen production.

Hydrogen produced from the SMR process includes small quantities of CO, CO_2, and HS as impurities and requires further purification. The primary steps for purification include:

1. **Feedstock purification:**

This process removes toxic substances, including sulfur (S) and chloride (Cl), to increase the life of the downstream steam reforming and other catalysts.

2. **Product purification:**

In a liquid absorption system, CO_2 is removed. The product gas undergoes a methanation step to remove residual traces of the carbon oxides. Recent SMR plants utilize a Pressure Swing Absorption (PSA) unit instead, producing 99.99 percent pure product hydrogen.

CURRENT STATUS

Steam reforming of natural gas is widely used in industry. Hydrogen is produced by the SMR process in large centralized industrial plants for use in numerous applications, including chemical manufacturing and petroleum refining. Research and development (R&D) programs are currently investigating the development of small-scale SMR technologies to enable the development of a small-scale, distributed hydrogen production and delivery infrastructure.

Steam reforming of natural gas offers an efficient, economical, and widely used process for hydrogen production, and provides near- and mid-term energy security and environmental benefits. The efficiency of the steam reforming process is about 65-75 percent, among the highest of current commercially available production methods.

Natural gas is a convenient, easy to handle, hydrogen feedstock with a high hydrogen-to-carbon ratio. It is also widely available from sources in the USA and Canada.

The cost of hydrogen produced by SMR is dependent on the natural gas prices and is currently the least expensive among all bulk hydrogen production technologies. A well-developed natural gas infrastructure already exists in the USA, a key factor that makes hydrogen production from natural gas attractive.

TECHNOLOGICAL HURDLES

During the production of hydrogen, CO_2 is also produced. The SMR process in centralized plants emits 2.51 times CO_2 than the hydrogen produced.

To avoid the emission of CO_2 into the atmosphere, it must be concentrated, captured, and sequestered.

The sequestration concepts and technologies are relatively new and there is no long-term test evidence to prove that these technologies will be successful. Sequestration in the oceans is controversial because of the possible adverse impact on the aquatic environment by the reduction of ocean water pH.

A problem with SMR is that it is operating at or near its theoretical limits; the hydrogen produced is still expensive compared to the USA Department of Energy's (DOE) cost targets for producing hydrogen for future automobiles and other applications.

Research and development aims at identifying more durable reforming catalysts; improve reforming efficiencies; develop advanced shift, separation, and purification technologies; and reduce the cost of carbon capture and sequestration.

If natural gas is used for hydrogen production, and the demand of natural gas in other market sectors continues to grow, the natural gas reserves would decrease and the supply will be put under greater pressure. This could result in increased natural gas prices.

Natural gas represents one of the viable pathways for introducing hydrogen as an energy carrier for a future USA hydrogen energy economy because it is among the least expensive feedstocks for producing hydrogen.

Carbon capture and sequestration is needed to eliminate the high level of greenhouse gas emissions associated with using natural gas.

The USADOE has a goal to reduce the cost of distributed hydrogen production from natural gas to \$1.50/kg H_2 by 2010 as well as improve efficiencies to 75 percent by 2010.

REFERENCES

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