

HYDROGEN PRODUCTION FROM FOSSIL FUELS

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Keywords: Steam reforming, parted oxidation, coal gasification, steam-iron process

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Summary

A review of conventional methods of production of hydrogen from fossil fuels is presented. Some advanced and unconventional methods of production of hydrogen based on fossil fuels are also presented. The general characteristics of the feedstocks used to produce hydrogen are first described. This is followed by the chemistry required to generate hydrogen. Then the chemical process operations and chemical engineering are detailed including process flow diagrams. A brief review of the efficiency and economics of the conventional fossil fuels is presented.

1. Introduction

Hydrogen was first identified by the English scientist Cavendish in 1776 when dissolving metals in dilute acids. Since the discovery, a number of chemical transformations were used to produce hydrogen in the laboratory and for small-scale usage. These included, among others, the electrolysis of water, the reaction of zinc with hydrochloric acid, the reaction of sodium with water, and the dissolution of aluminum or silicon in caustic alkali sodium hydroxide solutions. However, by far the greatest amount of hydrogen produced for industrial purposes is produced by the steam reforming of natural gas (methane). The reason for this is that natural gas is abundant, is available in most parts of the world, has the highest hydrogen content of all fossil fuels, and is of low cost. In terms of production capacity, the process second to steam reforming of methane for hydrogen production is the partial oxidation of petroleum oil. Following natural gas and oil is the process of steam gasification of coal. In these thermal fossil fuel processes, hydrogen is derived not only from the fossil fuels but also from the reaction with water, which must be added to the process.

In addition to the well-developed conventional processes mentioned above, other processes that have been practiced on an industrial scale are described. These include the steam-iron process and water electrolysis process. A number of advanced processes can be mentioned including the thermal cracking of natural gas and higher hydrocarbon fuels, the hydrocarbon coal process, coal gasification with electrochemical shift, high temperature electrolysis, and coal gasification with high temperature electrolysis.

There are also hydrogen by-product processes, which include hydrogen by-product from the production of electrolytic caustic-chlorine production, hydrogen from crude oil refining operations, hydrogen from coke oven gases, and hydrogen from hydrocarbon dehydrogenation processes. Hydrogen can also be produced by reforming ammonia and methanol.

Finally, water-splitting processes will be described in later articles; these include thermochemical processes, solar thermal processes, photochemical processes, high energy radiation processes, and biomass-based processes. This review has been mainly based on the two references, Steinberg (1989) and Czugson, Kenz, and Nerosome (1995).

2. Steam Reforming of Natural Gas (Methane)

The sequence of chemical reactions and the energetics for the steam reforming of methane as well as light gas oils, mainly naphtha, are as follows:

1. *Synthesis gas generation*: production of CO and H₂ by reaction of methane with steam.



The standard heat of reaction is +60 kcal mol⁻¹ endothermic.

2. *Water-gas shift*: reaction of CO with H₂O to produce CO₂ and more H₂.



The standard heat of reaction is 0 (neutral).

3. *Gas purification*: gasification includes acid gas removal, mainly CO₂, with a solvent such as an alkanolamine (MEA) or by pressure swing adsorption (PSA) with an adsorbent such as activated carbon. Residual CO maybe combined with hydrogen in a methanation reaction step to reform methane is recycled.

A detailed description of the process and the engineering parameters are described in the following.

For several decades, steam reforming of hydrocarbons has been the most efficient, economical and widely used process for production of hydrogen and hydrogen/carbon-monoxide gas mixtures. The process basically involves a catalytic conversion of the

hydrocarbon and steam to form hydrogen and carbon oxides. Since the process works only with light hydrocarbons, which can be vaporized completely without carbon formation, the feedstocks used range from methane, to naphtha to No. 2 or light fuel oil. Fifty percent of the hydrogen produced comes from the water (steam) when methane is used and 64.5% when naphtha is used.

A simplified basic flow diagram of the conventional steam reforming process is shown in Figure 1a. The process consists of three main steps: (1) synthesis gas generation, (2) water-gas shift, and (3) gas purification. To protect the catalysts in the hydrogen plant, the hydrocarbons have to be desulfurized before being fed to the reformer furnace. The desulfurized feedstock is then mixed with process steam and reacted over a nickel-based catalyst contained inside a system of high alloy steel tubes. The following reactions take place in the reformer:



where $n = 1$ and $m = 4$, if the hydrocarbon feedstock is methane, and $n = 1$ and $m = 2.2$, if it is naphtha. The reforming reaction is strongly endothermic, with energy supplied by radiant combustion of fuel gas or oil. The metallurgy of the tubes usually limits the reaction temperature to 760–925 °C (1400–1700 °F). At the same time, the CO shift and methanation reactions quickly reach equilibrium at all points in the catalyst bed. The equilibrium composition of the reformed gas is favored by high steam to carbon ration, low pressure, and high temperature. To ensure a minimum concentration of CH₄ in the product gas, the process generally employs a steam to carbon ratio of 3 to 5 at a process temperature of around 815 °C (1500 °F) and pressures up to 3.5 MPa (508 psi) to convert more than 80% of hydrocarbon to oxides of carbon at the outlet of the reformer. The typical composition (% by volume) of a synthesis gas at 100 psig leaving the steam-methane reformer is as follows:

Component	Vol. %
H ₂	74
CO	18
CO ₂	6
CH ₄	2
	100

After the reformer, the process gas mixture of CO and H₂ passes through a heat recovery step and is fed into a water-gas shift reactor to produce additional H₂. Normally, two stages of conversion (high temperature and low temperature) are used to reduce the CO content to a level of approximately 0.2–0.4 vol. %. This exothermic reaction occurs at temperatures ranging from 200 °C to 400 °C (392–752 °F).

The cold raw gases next pass through gas purification units to remove CO₂, the remaining CO, and other impurities to deliver the desired purified H₂ product to the

battery limits of the plant. Several commercial processes for removing CO_2 exist. One of these systems uses a wet scrubbing process, such as monoethanolamine (MEA), hot potassium carbonate, or sulfinol. The residual CO and CO_2 remaining in the H_2 stream after CO_2 removal are further converted to CH_4 by a methanation reaction. The product H_2 leaves with a purity of approximately 97–98%.

An alternate technology to wet scrubbing for removal of CO_2 is the use of the pressure swing adsorption (PSA) system. This process, shown in Figure 1b, reduces the number of unit processes and complexity of the operation by replacing the low temperature shift, the CO_2 removal, and the methanation units with a PSA process unit. In this process, the raw gas is passed through a series of beds of molecular sieves or activated carbon, where all components except H_2 are preferentially absorbed. The beds are regenerated by adiabatic depressurization at ambient temperature. The purge gas, which contains water vapor, CO_2 , CO and CH_4 , is then fed to the furnace for supplying heat to the reformer. The purity of H_2 from the PSA system can be 99% or higher, and can thus be used for a wide variety of chemical and petrochemical processes to considerable advantage.

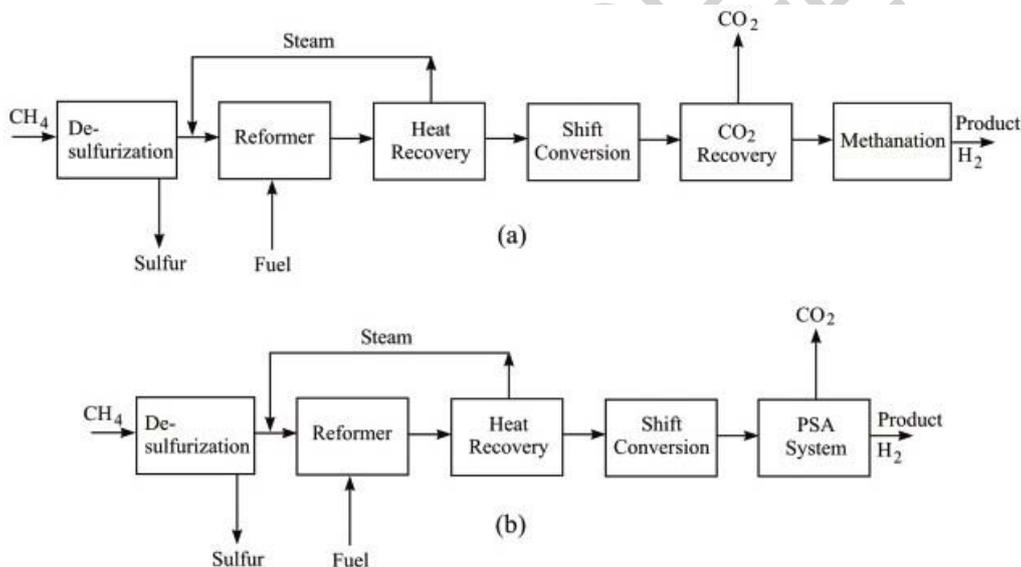


Figure 1. Simplified flow diagram of Hydrogen Production from Methane Steam Reforming
(a) Conventional Process, (b) with PSA modification.

In recent years advances in steam reforming have taken place to improve the efficiency and economics of hydrogen production. Direct fired tubular reformers have been the mainstay for hydrogen production. The main thrust has been in heat management which includes heat-exchange-based reforming, autothermal and secondary reforming, and adiabatic pre-reforming. Helium-heated reformers, electrically heated reformers, molten metal bath reformers, and pressurized fire box reformers have also been introduced. Integrated hydrogen separation reforming to obtain higher concentrations of hydrogen by shifting the equilibrium toward higher conversions using membranes has also been under development

The capacity of most steam reforming plants is in the range of $20\text{--}60 \times 10^6 \text{ SCF d}^{-1}$ (standard cubic feet per day). Single-train units are limited to $60 \times 10^6 \text{ SCF d}^{-1}$ by the size restriction of shop-fabricated construction of the reaction vessels. Economy of scale is essentially exhausted for a plant capacity of $100 \times 10^6 \text{ SCF d}^{-1}$. For capacities over $60 \times 10^6 \text{ SCF d}^{-1}$, the PSA process generally requires parallel trains or using an advanced design of polybeds.

A summary of the economics of hydrogen production of steam reforming and comparisons with other methods is given in Section 7.

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Biographical Sketch

Mr. Steinberg is a graduate professional chemical engineer of the Cooper Union, School of Engineering and Polytechnic Institute of Brooklyn. He worked on the Manhattan District's Atom Bomb Project and then as a chemical engineer in the heavy chemical and metallurgical industry. Since 1957 he has been at the Brookhaven National Laboratory. He has contributed to the field of radiation chemical processing and chemonuclear reactors. He is an inventor and developer of concrete polymer materials. His research in nuclear energy includes nuclear waste management and safety, the use of fission and fusion reactors for synthetic carbonaceous fuel production and the linear accelerator spallator for nuclear fuel production and transmutation of fission product waste and reduction of nuclear weapons materials. His research in fossil and solar energy involves coal conversion, desulfurization, hydrolysis, environmental control technologies for the global CO₂ problem and the conversion of biomass and municipal solid waste to clean fuels. Mr. Steinberg is a senior chemical engineer who, until recently, was Head of the Process Sciences Division of the Department of Applied Science at Brookhaven National Laboratory and presently is a senior chemical engineer in the Department of Advanced Technology. He is a fellow of the American Nuclear Society and the American Institute of Chemical Engineers and Emeritus member of the American Chemical Society. He has over 500 publications and holds 37 patents.