# HYDROGEN PRODUCTION BY STEAM REFORMING OF HYDROCARBONS

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## Introduction

The use of hydrogen for petrochemicals, fertilizers and as energy carrier in connection with renewable energy production will increase substantially in the next 5-10 years as even more stringent environmental legislation is enforced. Low sulfur gasoline and diesel fuels will become mandatory and harmful emissions will be reduced drastically. Hydrogen will be required by refiners and specialty chemical manufacturers to meet the global need for cleaner products. The growing fuel cell market will be dependant on hydrogen as a primary fuel source.

Hydrogen requirements vary widely. For small capacities below 0.1 MM SCFD, supply in cylinders or production by electrolysis may be preferable. Hydrogen production from methanol or ammonia cracking is suitable for small, constant or intermittent requirements as used in the food, electronics and pharmaceutical industries. For larger capacities hydrocarbons are used primarily as feedstock in the steam reforming process for production of hydrogen and synthesis gas.

The current production of hydrogen in North America is about 6000 MM SCFD, and the annual growth is expected to be above 4%. Most of this growth is for refineries for their production of ultra-low sulfur diesel and gasoline.

In spite of efforts to produce hydrogen by processes involving solar energy, wind energy, nuclear energy and biofuels, fossil fuels remain the most feasible feedstock in the near term, and for commercial scale production of pure hydrogen, steam reforming remains the most economic and efficient technology for a wide range of hydrocarbon feedstocks.

## Steam Reforming Technologies

A typical layout of a hydrogen plant based on steam reforming including the following steps:

Natural gas feed is preheated in coils in the waste heat section of the reformer, and sulfur is removed over a zinc oxide catalyst. Process steam is added, and the mixture of natural gas and steam is further preheated before entering the tubular reformer. Here, conversion to equilibrium of hydrocarbons to hydrogen, carbon monoxide and carbon dioxide takes place over a nickel based reforming catalyst.

The gas exits the reformer and is cooled by steam production before entering the shift converter, typically a medium temperature shift. Over the shift catalyst more hydrogen is produced by converting carbon monoxide and steam to carbon dioxide and hydrogen. The shifted gas is cooled further to ambient temperature before entering the PSA unit. High purity hydrogen product is obtained, and the off-gas from the PSA unit is used in the reformer as fuel supplemented with natural gas fuel.

Combustion air for the tubular reformer burners can be preheated in coils in the reformer waste heat section. Part of the steam produced in the hydrogen plant is used as process steam, the excess steam is exported.

In many situations when natural gas is not available, higher hydrocarbons become the preferred feedstock for the reforming process. Many refineries also can benefit from flexibility in feedstock, taking advantage of the surplus of various hydrocarbon streams in the refinery.

Fired tubular reforming is generally the most competitive technology for capacities of up to more than 100 MM SCFD hydrogen.

Topsoe's latest development in steam reforming process technology is the advanced steam reforming process. The characteristics of this process are:

- High reformer outlet temperature
- Low steam to carbon ratio.
- High combustion air preheat (optional).
- Adiabatic prereforming (optional).
- High heat flux reformer.

Low steam to carbon ratios, typically 2.5, in hydrogen plants, reduce the mass flow through the plant and thus the size of equipment. The lowest investment is therefore generally obtained for plants designed for low steam to carbon ratios. However, a low steam to carbon ratio also increases the methane leakage from the reformer. This can be compensated for by increasing the reformer outlet temperature to typically $1690^o$ F in hydrogen plants. Furthermore, operating at a low ratio requires the use of non-iron containing catalyst i.e. a copper-based medium temperature shift catalyst in order to eliminate production of by-products in the shift section.

The installation of an adiabatic prereformer upstream of a tubular reformer has been found to be very advantageous in naphtha based plants and plant operating on fuel gases with higher concentrations of higher hydrocarbons. Since all higher hydrocarbons are converted over the prereformer catalyst, the inlet temperature of the gas inlet in the reformer can be increased to $1200^o$ and the reformer can be designed for higher heat fluxes. This reduces the size of the tubular reformer, resulting in direct capital cost reduction.

High combustion air preheat temperatures results in reduced fuel consumption and reduced steam production. The combustion air temperature can be used to adjust the steam export to a desired level. Temperatures of up to $1020^o$ F are industrially proven in a radiant wall reformer.

The Topsoe convection reformer (HTCR) is a new concept which combines the radiant and waste heat section of the conventional reformer in one relatively small piece of equipment, thereby optimizing heat transfer to the steam reforming reaction and avoiding the surplus energy (often seen as steam export) inherent in conventional plants.

HTCR based layout is an attractive option for smaller sized hydrogen plants.

## Efficiency and Production Costs

With no steam export the theoretical energy consumption is 300 BTU/scf $H_2$ on LHV (lower heating value) basis. The industrial value for natural gas based plants is about 320 BTU/scf $H_2$ corresponding to 94% of the theoretical efficiency. At locations with high natural gas prices, the energy efficiency becomes critical. For a natural gas price of 4 USD/MM BTU, the feedstock and utility costs makes about 65% of total operating costs.

## Catalysts and the Mechanism of Steam Reforming

The steam reforming process may appear straightforward from an overall consideration as the product composition is determined

by simple thermodynamics, but in reality it is a complex coupling of catalysis, heat transfer and mechanical design.

In recent years, there has been progress in steam reforming technology resulting in less costly and more efficient plants, in part because of better materials for reformer tubes, better control and understanding of carbon limits, and better catalysts and process concepts with high feedstock flexibility. This progress has been accompanied by a better understanding of the reaction mechanism.

The typical steam reforming catalyst contains nickel. The catalyst properties are dictated by the severe operating conditions in the reformer with high temperatures and steam partial pressures. Sintering is an important cause of deactivation of nickel-containing steam reforming catalysts. The most important parameters are the temperature and the atmosphere in contact with the catalyst. The catalyst support can affect the sintering in various ways by loss of surface area. The sintering ceases when the nickel particle size exceeds a given size. The maximum size increases with temperature.

The catalyst activity is rarely a limiting factor. The catalyst volume (space velocity) is fixed from the tubular reformer design. The equilibrium conversion at high reforming temperatures is achieved at even very high space velocities when extrapolating the intrinsic rates. In practice, however, the utilization of the activity (as expressed through the effectiveness factor) is smaller than 10% because of transport restrictions. It can be shown by computer simulations that the catalyst is not the limiting factor for the design of a tubular reformer. An increase of the heat flux and the load at a given exit temperature by a factor of two results in an increase in methane leakage by only 10%.

Recent studies of the fundamentals of the steam reforming reactions have lead to a more consistent understanding of the mechanism of the main reactions and the competing reactions for carbon formation. The dissociation of methane on nickel surfaces has been investigated extensively, and several details of the reaction pathway are known from fundamental studies, in-situ high resolution electron microscopy and theoretical calculations.

In-situ high resolution electron microscopy has provided new information on sintering mechanisms and for the importance of steps in nucleation of whisker carbon. Density Functional Theory calculations have quantified the energetics of methane activation and shown that activation barriers are smaller on surface steps where also carbon is the most stable surface species.

**Conclusions**

The demand for hydrogen is growing in many industries, particularly in the chemical and refining industries. Topsoe has been active in this field for more than 50 years and offers a wide range of advanced technologies for small and large capacities meeting the demand for low operating and investment costs.

For small plants, convection reforming in the form of compact, skid-mounted plants is available. This is a low investment alternative to conventional concepts using tubular reforming.

For medium and large-scale plants the predominant technology is steam methane reforming of hydrocarbons. Advanced steam reformer design allows high temperatures and low steam to carbon ratios for hydrogen production resulting in high energy efficiency and lower cost plants.

For very large hydrogen and syngas plants the oxygen reforming technology may be applied, such as autothermal reforming and oxygen fired secondary reforming. These technologies are especially attractive when cheap oxygen is available.

**References**
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