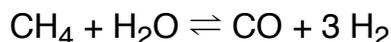


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# Steam reforming

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**Steam reforming** or **steam methane reforming** is a method for producing syngas (hydrogen and carbon monoxide) by reaction of hydrocarbons with water. Commonly natural gas is the feedstock. The main purpose of this technology is hydrogen production. The reaction is represented by this equilibrium:<sup>[1]</sup>



The reaction is strongly endothermic (consumes heat,  $\Delta H_r = 206$  kJ/mol).

Steam reforming of natural gas produces 95% of the world's hydrogen ( $\text{H}_2$ )<sup>[2][3]</sup> of 500 billion m<sup>3</sup> in 1998,<sup>[4]</sup> or 70 million tonnes by 2018.<sup>[5]</sup> Hydrogen is used in the industrial synthesis of ammonia and for the production of myriad other chemicals.<sup>[6]</sup>

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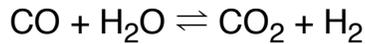
**References**

## Industrial practice

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The reaction is conducted in a reformer vessel where a high pressure mixture of steam and methane are put into contact with a nickel catalyst. Catalysts with high surface-area-to-volume ratio are preferred because of diffusion limitations due to high operating temperature. Examples of catalyst shapes used are spoked wheels, gear wheels, and rings with holes. Additionally, these shapes have a low pressure drop which is advantageous for this application.<sup>[7]</sup>

Via the water-gas shift reaction, additional hydrogen can be obtained by treating the carbon monoxide generated by steam reforming with water:



This reaction is mildly exothermic (produces heat,  $\Delta H_r = -41$  kJ/mol).

For every tonne of hydrogen produced this way, 9 tonnes of CO<sub>2</sub> are also produced.<sup>[5]</sup>

The United States produces 9–10 million tons of hydrogen per year, mostly with steam reforming of natural gas.<sup>[8]</sup> The worldwide ammonia production, using hydrogen derived from steam reforming, was 144 million tonnes in 2014.<sup>[9]</sup> The energy consumption has been reduced from 100 GJ/tonne of ammonia in 1920, to 27 GJ by 2019.<sup>[5]</sup>

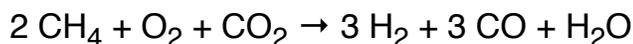
Steam reforming of natural gas is approximately 65–75% efficient.<sup>[10]</sup>

Production of H<sub>2</sub> and CO from hydrocarbon gases (e.g. natural gas) is performed by two well-known "primary" and "secondary" reformers. Steam methane reforming (SMR) and autothermal reformer (ATR) are two industrial examples of the primary and secondary reformers, respectively. On the other hand, the process of combined reforming utilizes both of primary and secondary tools for production of synthesis gas, as it is commonly practiced in ammonia manufacturing. For the case of methanol, ATR is fed with nearly pure oxygen (99.5%) rather than air since the presence of excessive N<sub>2</sub> in the syngas would overburden compression and retard the methanol production. The ATR reformer consists of a partial oxidation (POX) chamber (usually non-catalytic medium) and a fixed bed catalytic section. The catalytic fixed bed not only adjusts the H<sub>2</sub>/CO ratio, but also destroys any probable soot and precursor (e.g. ethylene and acetylene) that may be formed in the POX chamber. Natural gas (NG) is partially oxidized in the combustion chamber by oxygen or air (as an oxidant). Steam to carbon (S/C) ratio that is usually 0.6 in the oxygen-based case has been commercialized by Haldor-Topose Company.<sup>[11]</sup>

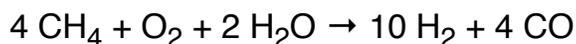
## Autothermal reforming

Autothermal reforming (ATR) uses oxygen and carbon dioxide or steam in a reaction with methane to form syngas. The reaction takes place in a single chamber where the methane is partially oxidized. The reaction is exothermic due to the oxidation. When the ATR uses carbon dioxide the H<sub>2</sub>:CO ratio produced is 1:1; when the ATR uses steam the H<sub>2</sub>:CO ratio produced is 2.5:1

The reactions can be described in the following equations, using CO<sub>2</sub>:



And using steam:



The outlet temperature of the syngas is between 950-1100 °C and outlet pressure can be as high as 100 bar.<sup>[12]</sup>

The main difference between SMR and ATR is that SMR only uses air for combustion as a heat source to create steam, while ATR uses purified oxygen. The advantage of ATR is that the H<sub>2</sub>:CO can be varied, which can be useful for producing specialty products. For example the production of dimethyl ether requires a 1:1 H<sub>2</sub>:CO ratio.

Although more costly to construct, SMR facilities produce hydrogen more cost-effectively than ATR facilities.<sup>[13]</sup>

## Partial oxidation

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Partial oxidation (POX) occurs when a substoichiometric fuel-air mixture is partially combusted in a reformer, creating a hydrogen-rich syngas. Being exothermic, POX is, typically, much faster than steam reforming and requires a smaller reactor vessel. As can be seen in chemical reactions of partial oxidation, this process initially produces less hydrogen per unit of the input fuel than is obtained by steam reforming of the same fuel.<sup>[14]</sup> Nevertheless, tendency to soot formation and relatively low hydrogen production yield are among the major drawbacks of this method.<sup>[15]</sup>

## Steam reforming at small scale

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The capital cost of steam reforming plants is considered prohibitive for small to medium size applications. The costs for these elaborate facilities do not scale down well. Conventional steam reforming plants operate at pressures between 200 and 600 psi (14 - 40 bar) with outlet temperatures in the range of 815 to 925 °C.

### For combustion engines

Flared gas and vented VOCs are known problems in the offshore industry and in the on-shore oil and gas industry, since both release greenhouse gases into the atmosphere.<sup>[16]</sup> Reforming for combustion engines utilizes steam reforming technology for converting waste gases into a source of energy.<sup>[17]</sup>

Reforming for combustion engines is based on steam reforming, where non-methane hydrocarbons (NMHCs) of low quality gases are converted to synthesis gas (H<sub>2</sub> + CO) and finally to methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>) and hydrogen (H<sub>2</sub>) - thereby improving the fuel gas quality (methane number).<sup>[18]</sup>

### For fuel cells

There is also interest in the development of much smaller units based on similar technology to produce hydrogen as a feedstock for fuel cells.<sup>[19]</sup> Small-scale steam reforming units to supply fuel cells are currently the subject of research and development, typically involving the reforming of methanol, but other fuels are also being considered such as propane, gasoline, autogas, diesel fuel, and ethanol.<sup>[20][21]</sup>

## Disadvantages

The reformer–fuel-cell system is still being researched but in the near term, systems would continue to run on existing fuels, such as natural gas or gasoline or diesel. However, there is an active debate about whether using these fuels to make hydrogen is beneficial while global warming is an issue. Fossil fuel reforming does not eliminate carbon dioxide release into the atmosphere but reduces the carbon dioxide emissions and nearly eliminates carbon monoxide emissions as compared to the burning of conventional fuels due to increased efficiency and fuel cell characteristics.<sup>[22]</sup> However, by turning the release of carbon dioxide into a point source rather than distributed release, carbon capture and storage becomes a possibility, which would prevent the carbon dioxide's release to the atmosphere, while adding to the cost of the process.

The cost of hydrogen production by reforming fossil fuels depends on the scale at which it is done, the capital cost of the reformer and the efficiency of the unit, so that whilst it may cost only a few dollars per kilogram of hydrogen at industrial scale, it could be more expensive at the smaller scale needed for fuel cells.<sup>[23]</sup>

## Challenges with reformers supplying fuel cells

However, there are several challenges associated with this technology:

- The reforming reaction takes place at high temperatures, making it slow to start up and requiring costly high temperature materials.
- Sulfur compounds in the fuel will poison certain catalysts, making it difficult to run this type of system from ordinary gasoline. Some new technologies have overcome this challenge with sulfur-tolerant catalysts.
- Coking would be another cause of catalyst deactivation during steam reforming. High reaction temperatures, low steam-to-carbon ratio (S/C), and the complex nature of sulfur-containing commercial hydrocarbon fuels make coking especially favorable. Olefins, typically ethylene, and aromatics are well known carbon-precursors, hence their formation must be reduced during the SR. Additionally, catalysts with lower acidity were reported to be less prone to coking by suppressing dehydrogenation reactions. H<sub>2</sub>S, the main product in the reforming of organic sulfur, can bind to all transition metal catalysts to form metal–sulfur bonds and subsequently reduce catalyst activity by inhibiting the chemisorption of reforming reactants. Meanwhile, the adsorbed sulfur species increases the catalyst acidity, and hence indirectly promotes coking. Precious metal catalysts such as Rh and Pt have lower tendencies to form bulk sulfides than other metal catalysts such as Ni. Rh and Pt are less prone to sulfur poisoning by only chemisorbing sulfur rather than forming metal sulfides.<sup>[24]</sup>

- Low temperature polymer fuel cell membranes can be poisoned by the carbon monoxide (CO) produced by the reactor, making it necessary to include complex CO-removal systems. Solid oxide fuel cells (SOFC) and molten carbonate fuel cells (MCFC) do not have this problem, but operate at higher temperatures, slowing start-up time, and requiring costly materials and bulky insulation.
- The thermodynamic efficiency of the process is between 70% and 85% (LHV basis) depending on the purity of the hydrogen product.

## See also

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- Biogas
- Catalytic reforming
- Chemical looping reforming and gasification
- Cracking (chemistry)
- Hydrogen pinch
- Hydrogen technologies
- Industrial gas
- Lane hydrogen producer
- Methane pyrolysis
- Partial oxidation
- PROX
- Reformed methanol fuel cell
- Reformer sponge iron cycle
- Timeline of hydrogen technologies

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