



OVERVIEW OF HYDROGEN PRODUCTION METHODS

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Prepared by WG-14 – Hydrogen Production

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1 Introduction

There has been a recent increase in interest in the topic of hydrogen production, from many sectors, as hydrogen users shift from traditional operators such as refineries or industrial gas companies using conventional carbon feedstock based hydrogen production processes to clean energy users needing hydrogen with low or zero carbon footprint. There is an urgent need to decarbonise energy production, with increasing demand for hydrogen as a feedstock and for energy uses. Many new hydrogen production facilities are forecast to be needed to fulfil this increasing demand. There was a gap in existing texts, with no simple comparative overview available of all commercial scale hydrogen production methods, so this EIGA document was produced to fill that gap.

2 Scope and purpose

2.1 Scope

This publication covers current commercially available industrial hydrogen production methods.

2.2 Purpose

The purpose of this document is to provide an accessible overview of current commercially available industrial hydrogen production methods.

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publication terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions

AEL – Alkaline Electrolysis
ATR – Auto Thermal Reforming
DIW – De Ionised Water
GHG – Green House Gas
HyCO – Hydrogen & Carbon Monoxide Production Plant
LCA – Life Cycle Assessment
LHy – Liquid Hydrogen

aMDEA – Activated Methyldiethanolamine
MDEA – Methyldiethanolamine
LPG – Liquefied Petroleum Gas
POX – Partial Oxidation
PCF – Production Carbon Footprint
PEM – Proton Exchange Membrane Electrolysis
PSA – Pressure Swing Adsorber
SMR – Steam Methane Reforming
Syngas – Synthesis Gas

3.2.1 Pressure

In this publication bar shall indicate gauge pressure unless otherwise noted i.e. (bar, abs) for absolute pressure and (bar, dif) for differential pressure.

4 Direct H₂ Production

4.1 Steam Methane Reforming (SMR)

Steam methane reforming (SMR) is a well-established, industrial process for the large-scale production of hydrogen. The SMR process involves the conversion of a hydrocarbon feedstock with steam to hydrogen through catalytic reactions. Most commonly methane is used as a feedstock but alternatively heavier hydrocarbons up to naphtha can serve.

Typically in a traditional SMR process, all the carbon within the feedstock and fuel is ultimately emitted to the atmosphere as carbon dioxide hence hydrogen from a SMR is usually considered to be “[Grey Hydrogen](#)”; however there is a drive towards using SMR process technologies where this carbon is captured from within the process for sequestration, thus becoming “[Blue Hydrogen](#)”, see [Section 6 for Carbon Capture Technologies](#) and see [Section 9 on Carbon Intensity](#).

Until recently SMR has been the dominant technology for hydrogen production, given the competitive production cost as well as the widespread availability of natural gas and higher hydrocarbons as a feedstock, and it continues to play a role in meeting the demand for hydrogen across industrial sectors.

The steam methane reforming process can be broken down into the following steps:

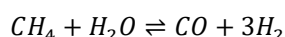
Feed purification and pre-heat

Prior to the main steam methane reforming process, the feedstock must be initially purified to eliminate harmful contaminants, particularly sulphur and chloride compounds. Usually this is achieved by passing the feedstock through a hydrogenator reactor then absorbers, where impurities are hydrogenated then absorbed. Alongside this, water is purified in preparation for raising steam for the reactions. Steam is injected to the feed gas downstream of the feed purification section at an optimal ratio.

Reforming reaction

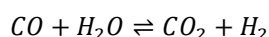
If the feedstock includes heavier hydrocarbons, it can be preferable to include a pre-reforming step, this reduces the duty in the main reformer leading to lower operating costs and can extend the life of the main reformer catalyst. The pre-reforming reaction occurs in a fixed bed reactor where the heavy hydrocarbons react to form methane. If using a natural gas feedstock this step can be omitted.

The methane and steam mix pass to the main reformer where, promoted by the catalyst, it undergoes a strongly endothermic reaction resulting in a synthesis gas mixture comprising mainly hydrogen and carbon monoxide. The main reaction can be represented by the equation:



Water Gas Shift Reaction

To improve the yield of hydrogen, the residual steam and carbon monoxide present in the gas mixture from the reforming step can undergo an additional reaction known as the water gas shift reaction. This reaction is employed to further enhance the hydrogen content in the final product. The main water gas shift reaction is represented by the equation:



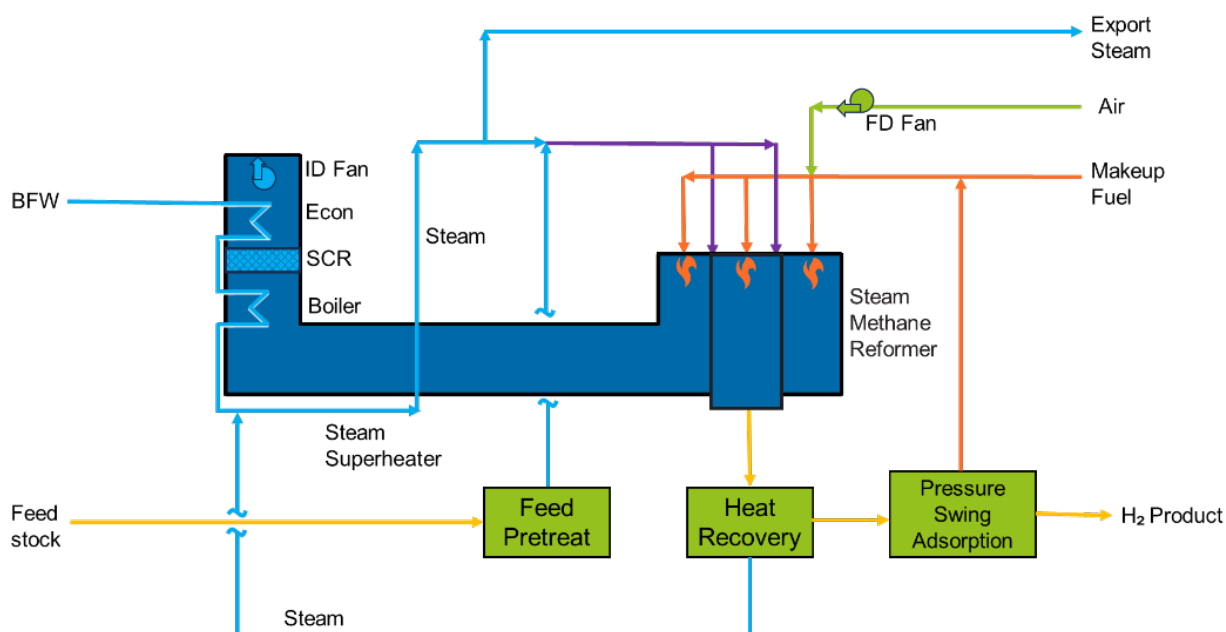
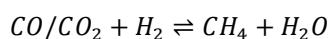
Heat Recovery

The upstream reactions yield a saturated syngas mixture comprising mainly hydrogen, carbon monoxide, steam/water, residual amounts of methane and trace quantities of other substances such as carbon dioxide, plus inert gases such as nitrogen and argon if these were present in the feed. This syngas stream is cooled in stages, with heat being recovered to raise steam for the reaction, and pre-heat the various feed and reformer fuel and combustion air streams. Residual water in the syngas condenses and is collected for recycling back to the main process steam system.

Product purification

To ensure the high purity of the hydrogen product gas the syngas stream further undergoes a further purification process, typically in a multi-bed PSA ([see section 5.1 for more on PSA's](#)), this removes many residual impurities, including carbon monoxide, carbon dioxide, nitrogen, methane, and water. The impurities are removed as a low-pressure off-gas stream which is returned to the main reformer, where it meets most of the process requirements for fuel.

For further removal of low ppm levels of carbon oxides in the product hydrogen, for example to produce fuel cell specification hydrogen, an additional methanation step can be beneficial. The methanation reaction is represented by the equation:

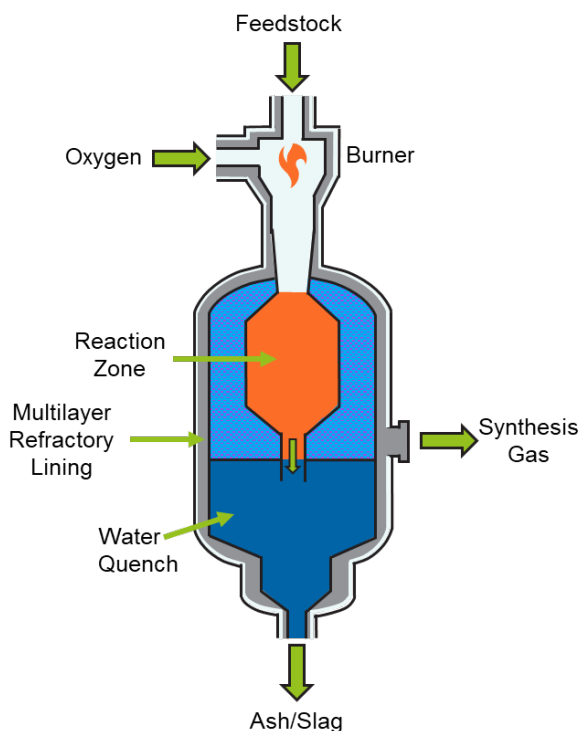


[Figure 1 – Schematic of a typical SMR plant]

See also EIGA Doc 242, [1] “Safety of Hydrogen, HYCO Production and Carbon Capture”, EIGA Doc 246 [2] “Guideline for Small Scale Hydrogen Production”, EIGA Doc 155 [3] “Best Available Techniques for Hydrogen Production by Steam Methane Reforming” and EIGA Doc 230 [4] “Safe Catalyst Handling in HyCO Plants.”

4.2 Partial Oxidation (POX)

For many decades Partial Oxidation (POX) represents a matured and well-known industrial process for a broad range of syngas production applications. Due to its required substantial capital investment, it is usually applied for medium to large scale syngas applications.



[Figure 2 Schematic overview of POX reactor]

Hydrocarbon feedstock is fed via a burner/feed injector into a reaction chamber within a refractory lined vessel. Across the reaction zone, the hydrocarbon feedstock reacts in under-stoichiometric conditions with a co-injected oxidant (typically pure oxygen) and forms syngas, a mixture consisting mainly of hydrogen and carbon monoxide. The typical operating pressure of POX units covers a range of 40 to 100 barg.

The overall POX process is called auto-thermal and proceeds exothermally, hence there is no need for an external heat supply. Feedstock and Oxygen are typically preheated before injection.

The different reactions, that occur simultaneously within the reaction zone, can be clustered as follows:

Hydrocarbon conversion



Combustion reactions



Homogeneous gas phase reactions



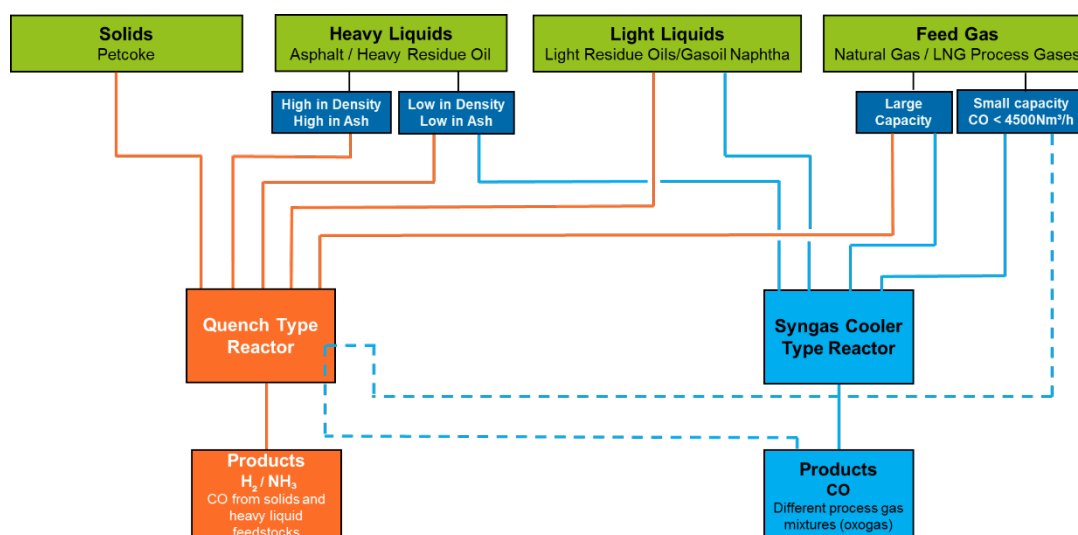
Heterogenous gas-solid reactions



Equation (1) shows the desired reaction where hydrocarbons are partially oxidated towards hydrogen (H_2) and carbon monoxide (CO). The exothermic combustion reactions **(2)**, **(3)** and **(4)** are providing the heat for the POX reactor by full oxidation of contained methane, hydrogen, and carbon monoxide to carbon dioxide (CO_2) and steam (H_2O). **Equation (5)** is representing the water-gas shift reaction, which shows the equilibrium for shifting carbon monoxide by steam towards carbon dioxide and hydrogen. For higher temperatures the equilibrium of water-gas shift reaction is favouring the carbon monoxide production. **Equation (6)** represents the hydrocarbon steam reforming equation, which converts hydrocarbons by steam to hydrogen and carbon monoxide. Especially the equilibrium of the heterogenous gas-solid reactions, i.e. the soot formation, is dependent on the feedstock used for the process.

Due to the absence of catalyst, syngas production via Partial Oxidation is quite robust and flexible regarding feedstock type and quality. Typical applications cover the processing of coal, liquid feedstocks such as oil or heavy hydrocarbon residues and lean gaseous feeds like natural gas. But partial oxidation strictly requires a proper mixing of the reactants and high reaction temperature (approx. 1400 °C) to ensure complete carbon conversion and to reduce soot formation especially for heavy feedstocks. Sometimes steam addition as moderating agent is required to suppress carbon formation.

The hot syngas leaving the POX reactor must be cooled in a further process step. The selection of syngas cooling concept is critical and depending on feedstock and project specifics. Below **Figure 3** gives an overview about the syngas cooling selection and some typical feedstocks used for syngas generation via POX:



[Figure 3 Syngas cooling depending on feedstock and its tendency of soot formation]

Since there is no external fired heater or similar required, there are no direct gaseous emissions related to the operation of such a device. Depending on the finally required syngas composition, there might be direct emissions (if they can be used: co-products) like carbon dioxide leaving a downstream CO_2 capture unit in case this is applied. Another effluent leaving the process is the ash/slag solution, again highly depending on the feedstock, its tendency for soot formation and on the applied syngas cooling concept.

Benefits

- Carbon capture is easier as CO_2 is completely contained within the process stream, (no separate flue gas as exists as in the SMR process).
- A very wide range of feedstocks can be processed, including heavy (high carbon content).