



BEST AVAILABLE TECHNIQUES FOR HYDROGEN PRODUCTION BY STEAM METHANE REFORMING

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Prepared by AHG-5.1 of WG-5 Environment

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Amendments to Doc155/09

Section	Change
all	Complete rework of Doc155.
all	Integration of Doc183/13 “ <i>Best Available Techniques for the Co-Production of Hydrogen, Carbon Monoxide & their Mixtures by Steam Reforming</i> ” into this Doc155. Doc183 is withdrawn.

1 Introduction

This EIGA publication provides guidance to EIGA members, specifically to site managers, technical managers, and company environmental specialists on best available techniques for the production of hydrogen, or the co-production of hydrogen, carbon monoxide and their mixtures by steam methane reforming. It is intended to support and complement the EU Best Available Technique (BAT) reference documents (BREF) (REF [*REFineries*], LVOC [*Large Volume Organic Chemicals*], LVIC [*Large Volume Inorganic Chemicals*], WGC [*Waste Gas Chemicals*]) by the European Integrated Pollution Prevention and Control Bureau (EIPPCB). This publication has been updated and also incorporates EIGA Doc 183, *Best Available Techniques for the Production of Hydrogen, the Co-Production of Hydrogen, Carbon Monoxide and their Mixtures by Steam Methane Reforming* [1].¹ (withdrawn).

2 Scope and purpose

This publication covers guidance on compliance with Directive 2010/75/EU, *Industrial Emissions Directive* (IED) and associated BREFs [2]. The main objectives are to:

- contribute to the EIPPCB's reference documents that are associated with hydrogen, carbon monoxide and syngas production technologies;
- propose techniques deemed as best and available for steam methane reformer plants with one or multiple products;
- document data to support conclusions on BATs; and
- encourage consistency with associated BREFs about hydrogen, carbon monoxide, and syngas production.

This publication addresses both the steam reforming where hydrogen (besides the co-produced steam) is the only product, as well as the co-production of hydrogen, carbon monoxide, and their mixtures by steam reforming. The main focus of this document is large plants with production of gaseous hydrogen greater than 10 000 Nm³/h (based on EIPPCB's *Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas* [3]. For plants producing hydrogen and carbon monoxide, this threshold should be considered as the sum of hydrogen, carbon monoxide and syngas production. For other plants some BAT may not be applicable for technical and economic reasons.

Hydrogen liquefaction is not addressed in this publication. Hydrogen will always refer to gaseous hydrogen.

This publication does not address small plants less than 2 tonnes per day (less than 1000 Nm³/h hydrogen), which are covered in EIGA Doc 220, *Environmental Guidelines for Permitting Hydrogen Plants Producing Less Than 2 Tonnes Per Day* [4].

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.

¹ References are shown by bracketed numbers and are listed in order of appearance in the reference section.

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

3.2.1 HyCO

Refers to the entire process in Figures 2, 3, 4, 5, 6 and 7. For the purpose of this publication, HyCO is used for the production of any or all of the products (hydrogen, carbon monoxide and / or syngas). Where techniques are applicable to hydrogen production only as standalone this will be identified in the text.

3.2.2 Steam methane reformer

Processing unit where steam is reacted with hydrocarbons over a catalyst at high temperatures to produce hydrogen and carbon oxides.

The reformer includes a furnace / radiant section and a convection section.

3.2.3 Syngas

Mixtures of hydrogen and carbon monoxide are called synthesis gas or syngas for short. As a matter of convention, this publication will call the production and / or co-production of these products HyCO production.

4 Production of hydrogen and co-production of hydrogen, carbon monoxide and syngas by steam reformers and coldbox

4.1 General

Hydrogen, carbon monoxide, and their mixtures may be co-produced through any one of a number of chemical processes that use hydrocarbon feedstock and a fired reactor. These process technologies include:

- steam reforming of light feedstock (for example methane or naphtha);
- auto-thermal reforming; or
- gasification / partial oxidation of heavier hydrocarbons.

In addition to hydrogen, carbon monoxide and syngas, these processes also produce steam and carbon dioxide. Steam generation results from heat recovery from the hot process gases downstream of the fired reactor and from hot flue gases.

The ultimate choice of process technologies depends primarily on the desired split of hydrogen and carbon monoxide product and secondarily on the available feedstock. This hydrogen / carbon monoxide

split (H_2/CO ratio) is driven by the customer(s) and the intended industrial application(s). This co-production means that products can be supplied to multiple industrial customers from diverse industrial sectors. As a result, the H_2/CO product split can vary drastically from installation to installation. For the remainder of the publication, we assume that the H_2/CO split is a predefined design objective which is fixed by the customer(s). It is not an independent variable that designers can arbitrarily change. Figure 1 shows the typical H_2/CO product split ranges for steam reforming, auto-thermal reforming, and partial oxidation. It also includes the range for two step-reforming where any of the above processes are followed by a heat-exchange type reformer.

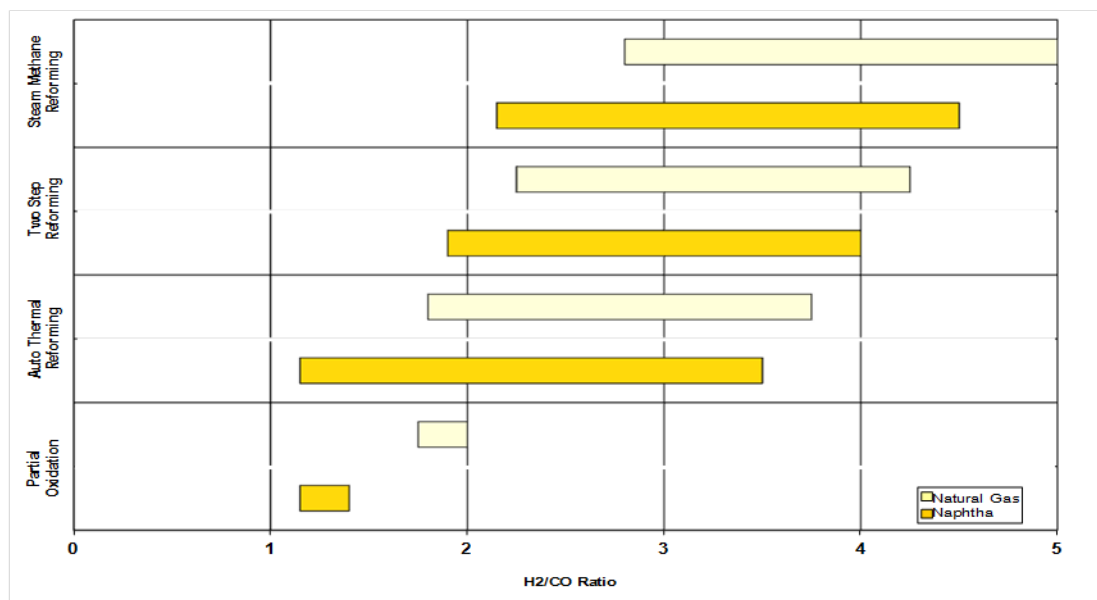


Figure 1 – H_2/CO split for HyCO process technologies [5]

This publication seeks to focus solely on the steam reforming process because of the wide coverage of H_2/CO split. Normally steam reforming results in a H_2/CO ratio of about five. By recycling the carbon dioxide, separated in a chemical wash unit, the H_2/CO ratio can be reduced to a value of approximately three. If a lower H_2/CO ratio is required, additional carbon dioxide can be imported. Hence HyCO plants including steam reforming enables a very flexible plant operation.

This publication describes the relative environmental impacts and advantages of steam reforming as a process choice and then describes some of the best available techniques that may be used to improve its environmental performance.

4.2 The steam methane reforming process

The steam reforming process can be used quite flexibly to address a wide range of H_2/CO product splits. This design objective is achieved by selecting from a number of pieces of process equipment. They are typically:

- feed pre-treatment unit steam methane reformer (SMR);

NOTE Pre-reforming is addressed in 6.3.

- carbon monoxide shift unit;
- carbon dioxide removal by chemical wash;
- dryers and cold box;
- pressure swing adsorption (PSA); and

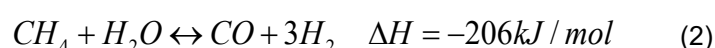
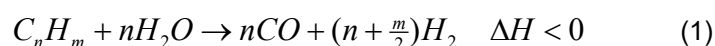
- membranes.

This section first describes the function of each piece of equipment and then provides a number of indicative process flows to demonstrate the flexibility of the process.

4.2.1 Steam reforming process equipment

Desulphurisation unit: the first piece of process equipment is a desulphurisation unit. The catalysts used in the downstream steam reformer box are particularly vulnerable to sulphur poisoning, therefore the feedstock must first be desulphurised.

Steam methane reformer: next, the steam reformer takes the desulphurised feedstock and provides the principle step of the process:



These reactions apply for either methane or heavier feedstock [6]. These reactions are achieved by passing the steam / feedstock mixture through the reformer tubes filled with a (usually nickel-based) catalyst at high temperature. Higher temperatures give greater yields but use of higher temperatures is limited by availability of temperature resistant materials and has an impact on NOx production.

Because the first two reactions dominate, the reaction overall is highly endothermic and reformer gas outlet temperatures are in the range of 820-1000 °C. The heat necessary to compensate for the overall endothermic reaction is radiated to the reformer tubes by burners that may be mounted on the top, side or bottom walls of the reformer box. The burners may use as a fuel a combination of the feedstock, other fuel gas(es), and Pressure Swing Absorption (PSA) tail gas.

Shift reactor: the shift reactor(s) increase the hydrogen product by shifting carbon monoxide into hydrogen according to reaction (3). It may be added to the main line to adjust the product split (see Figure 3 for example). In comparison to the SMR, the reaction occurs at a lower temperature in the range of 200-450 °C in the presence of a catalyst (for example iron-chromium, copper alloys) [7]. Depending on the operating temperature range, the shift reactor may be called high temperature (HT), medium temperature (MT), or low temperature (LT). A HT and LT reactor may be used in a serial fashion.

Carbon dioxide removal by chemical wash: from a process point of view, the carbon dioxide removal unit serves three purposes. First, the downstream cold box requires carbon dioxide-free process gas. If carbon dioxide remains in the process gas, it will freeze inside the cold-box and cause blockage. Second, the extracted carbon dioxide may be used as a product in the event that there is demand for its use. Finally, in the event that the required H₂/CO ratio is particularly low, this carbon dioxide can be recycled to the reformer as a feedstock to produce additional carbon monoxide. Typically, the carbon dioxide content in the process gas is removed by chemical wash. A number of solvents like aqueous solutions of amines (for example MDEA, MEA, aMDEA²) may be used to complete the chemical wash. However, aMDEA is most commonly used in modern plants for its greater energy efficiency.

Adsorbers (dryers) and coldbox: process gas passes through adsorbers (dryers) to remove traces of water and carbon dioxide. The cold box uses a cryogenic distillation process to separate carbon monoxide from the process gas with a high yield. While carbon monoxide is leaving the cold box at product quality, hydrogen still contains impurities which may require further purification. An off-gas stream rich in hydrogen and methane coming out of the cold box is often recirculated back to the steam reformer as a fuel or as feedstock.

² MDEA or Methyl diethanolamine, MEA or monoethanolamine, aMDEA or activated MDEA.

Pressure swing adsorption: the PSA serves to purify the hydrogen or raw syngas stream, producing a pure hydrogen stream and a tail gas stream. The PSA tail gas contains the impurities removed from the raw hydrogen or syngas, primarily carbon monoxide, hydrogen, methane, carbon dioxide and water, and is usually fed to the reformer as the main fuel [7].

Membranes: in combination with the above techniques, membranes are used for adjusting the H_2/CO split of syngas delivered to specific consumers requirements. Membrane technology is a non-cryogenic gas separation process based on selective permeation. A syngas mixture is fed on the outside of the fibres, H_2 permeates to the inside and is recovered at low pressure.

4.3 Indicative process flow diagrams for HyCO production

The steam reforming process uses these pieces of process equipment to produce as many of the following as there is demand: hydrogen, carbon monoxide, steam, carbon dioxide, syngas. It is not uncommon to have two or three co-produced products. In all cases, a light hydrocarbon feedstock such as natural gas or naphtha is required. This section aims to provide some indicative examples of process flow diagrams to demonstrate the flexibility of the process. The appendix contains a simplified process model which illustrates the variety of hydrogen production parameters and their relative environmental impact.

Figures 2 and 3 demonstrate a typical process flow to produce pure hydrogen and steam (Figure 2) and for the co-production of hydrogen, carbon monoxide and steam (Figure 3). Steam is produced by heat recovery with the hot process gas plus hot flue gas.

In the former case, the process gas from the steam reformer passes through a shift reactor where more steam helps to convert more of the carbon monoxide content into more hydrogen.

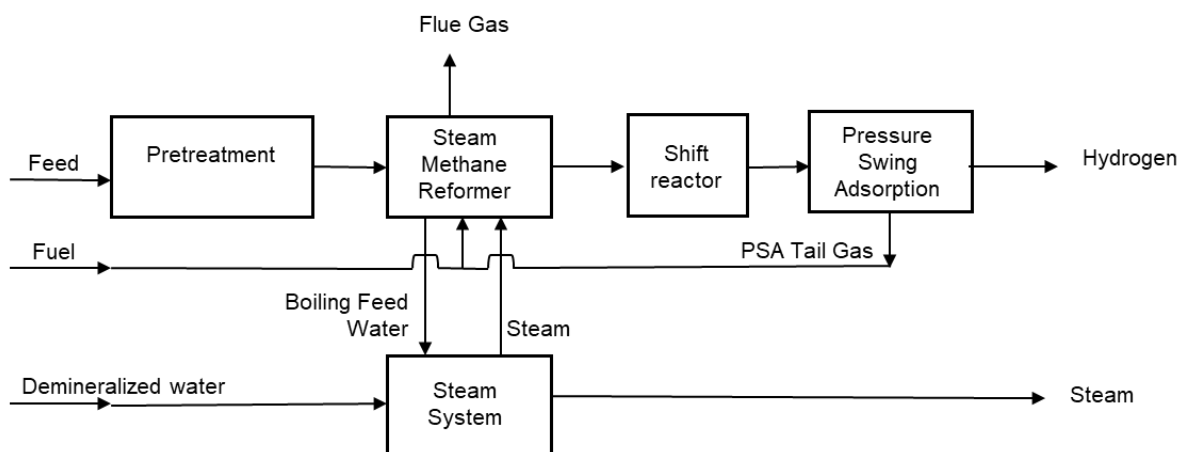


Figure 2 – Production of pure hydrogen and steam

In Figure 3, the process gas from the steam reformer is sent directly to a carbon dioxide removal unit, further the carbon monoxide is separated by cold box and the recovered hydrogen is purified by PSA. Depending on the required H_2/CO split, carbon dioxide may be fed back to the reformer as feedstock to increase carbon monoxide yield.

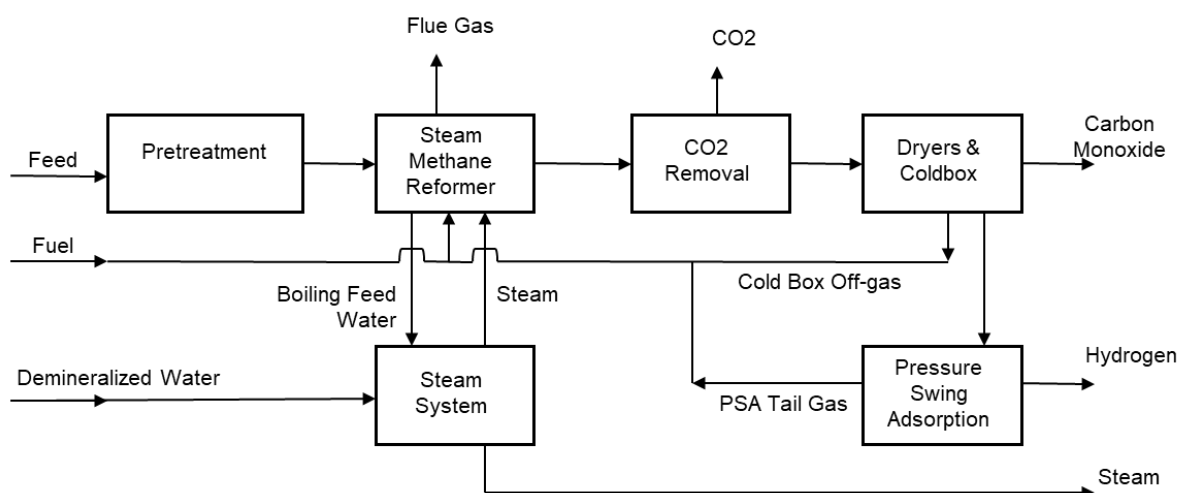


Figure 3 – Co-production of hydrogen, carbon monoxide and steam

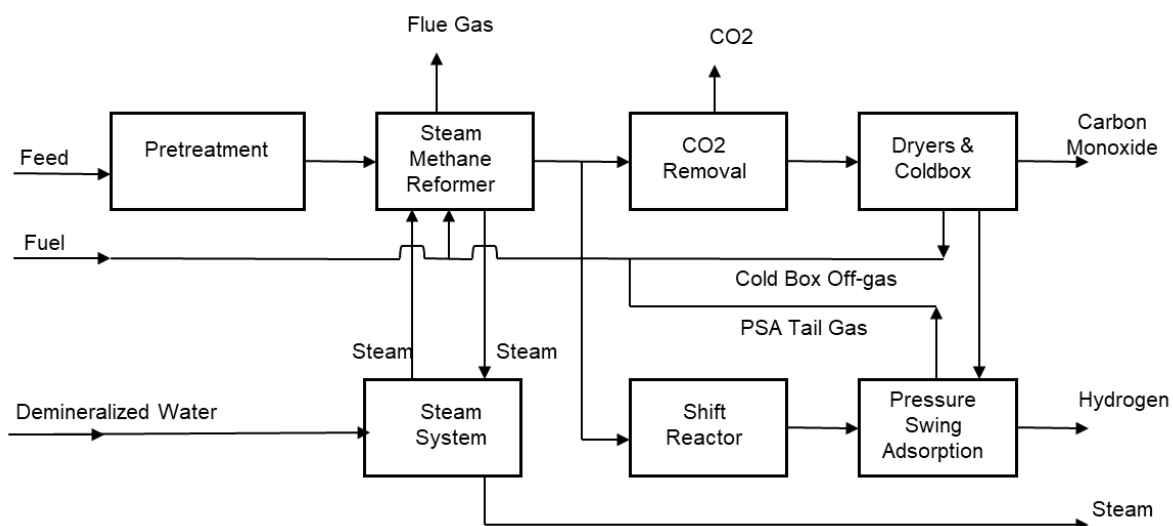


Figure 4 – Co-production of hydrogen, carbon monoxide and steam along with a shift reactor

Figure 4 adds a shift reactor in parallel to carbon dioxide removal. This serves to increase the H₂/CO ratio compared to the design shown in Figure 3.

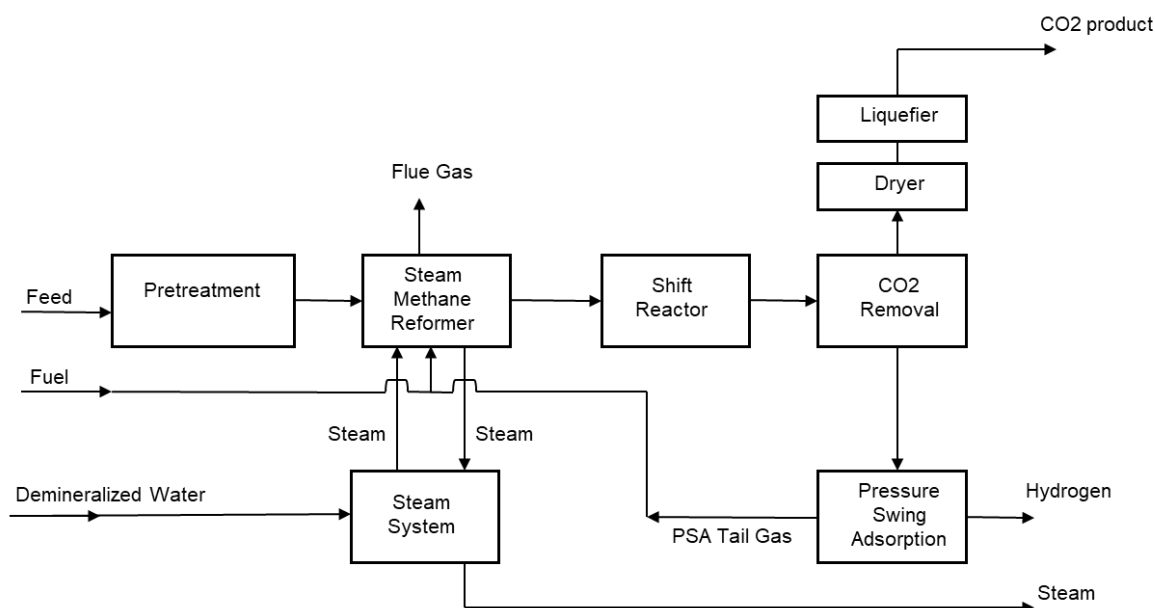


Figure 5 – Co-production of hydrogen and steam with complementary carbon dioxide production

Figure 5 is a special case where in addition to hydrogen and steam production, carbon dioxide is produced. In this case, there is no cold box, but rather a carbon dioxide removal unit downstream of the steam methane reformer and the shift reactor.

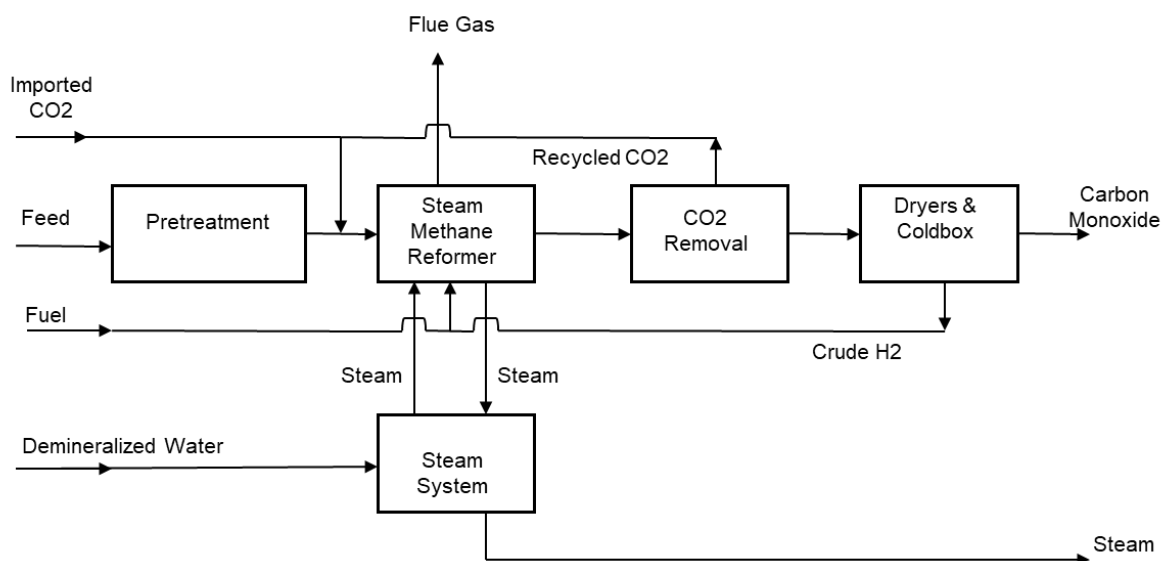


Figure 6 – Production of carbon monoxide and steam

Figure 6 demonstrates the case where only carbon monoxide is produced. The carbon dioxide removed from the carbon dioxide removal system is recycled back to the steam reformer as a feed and, if necessary, carbon dioxide may be imported from outside the battery limit of the plant. In this case, off-gas from the cold box has a large quantity of hydrogen (amongst other constituent gases), and its heating power is used in the fuel stream.

NOTE Hydrogen recycle to the desulphurisation unit as represented here applies also to any other scheme.

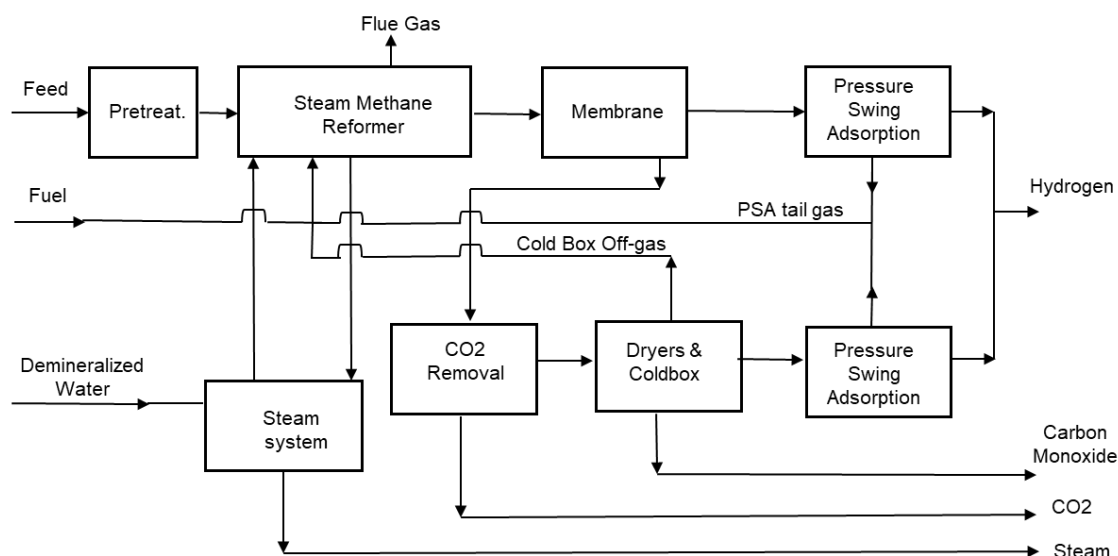


Figure 7 – Use of membrane in hydrogen and carbon monoxide production

Figure 7 demonstrates the use of membranes to obtain a CO₂ and CO-rich stream prior to final treatment. Such a scheme may require additional compression power to compensate membrane pressure drop ahead of the PSA.

4.4 Steam methane reforming process: environmental advantages and impacts

The choice of steam reforming comes with a number of associated environmental advantages and impacts relative to other processes. A more comprehensive treatment of the environmental impact of steam reforming and other hydrogen production techniques is found in EIGA Doc 122, *Environmental Impacts of Hydrogen Plants* [8]. First, the process generates few wastes, chemical storage, or liquid effluents. Section 6 describes good practice to limit these environmental aspects while Section 8 introduces elements of an appropriate environmental management system.

Steam reforming is the most commonly used method for hydrogen production at larger scale (greater than 10 000 Nm³/h). In some refineries, heavy oil residues are transformed into petroleum coke and subsequently gasified, or heavy oil residues are gasified directly to produce syngas.

Hydrogen can also be produced by electrolysis of water however this is currently not economic for large scale production. Hydrogen is also a coproduct of chlorine production by chlor-alkali electrolysis, this method is covered in BREF on production of chlor-alkali (CAK) [9].

Steam reforming is also advantageous from a product yield and energy consumption point of view. Figure 1 shows the product yield ranges for four industrial processes in terms of the ratio of hydrogen to carbon monoxide.

Common feedstocks for steam reforming are light, saturated hydrocarbons that are low in sulphur, this includes natural gas (the most common), refinery off-gas, LPG, and light naphtha. Steam reforming reduces the potential for carbon dioxide emissions with its requirement for lighter feedstock. Depending on the plant configuration to customer demand, carbon dioxide produced in a HyCO steam reforming process can be recycled into the process in order to increase CO yield.

Steam reforming can be used within an industrial complex to export steam as a valuable product, thereby eliminating the need for dedicated steam production elsewhere. This translates directly into energy and carbon dioxide emissions savings [7].

Steam methane reforming of natural gas typically has the smallest carbon-footprint of all hydrogen production processes, assuming that both direct and indirect emissions are counted, and that the energy mix of electricity production of the EU is used [10]. Nevertheless, in the absence of co-production

synergies, Reactions 2 and 3 show that by mass balance the process is limited to emit at least one mole of direct CO₂ for every four moles of hydrogen produced. (see the example in Appendix A) or, in other terms, emits one mole of direct CO₂ for every mole of carbon in the feedstock.

The remaining air emissions can be addressed individually.

The use of light hydrocarbon feedstock, and natural gas in particular, reduces the potential for particulates and SO_x emissions. SO_x emissions are reduced due to the necessary presence of the desulphuriser to eliminate the sulphur which would poison the SMR catalyst [10].

The process need for highly elevated temperatures increases the potential for NO_x emissions [11]. NO_x abatement measures are described in the following sections.

5 Best available techniques

5.1 Process techniques

5.1.1 Membranes

Description

Membrane technology is a non-cryogenic gas separation process based on selective permeation through a polymer material that acts like a filter. A membrane module consists of thousands of hollow fibres (200 to 450 µm diameter), formed into bundles and contained in a protective outer shell. In addition, pre-heater, coalescer and coolers are required. A syngas mixture is fed on the outside of the fibres, hydrogen permeates to the inside and is recovered at low pressure with purity up to 99 %.

Applicability

Membranes are used for adjusting the H₂/CO ratio of syngas delivered to specific consumers requirements, such as: Oxo-alcohols (H₂/CO = 1-1.3), Butane-diol production (H₂/CO = 1.6) or Fischer-Tropsch GTL processes (H₂/CO = 1.96).

Membranes are also used for carbon monoxide cold box debottlenecking.

Achieved environmental benefits

- Reduced heat load: hydrogen in excess is not flared but sent back to burners which reduces the amount of fuel gas.
- Reduced energy consumption: carbon monoxide cold box duty is reduced and hence this reduces energy consumption of the carbon monoxide compressor for certain syngas products or H₂/CO split.

Cross-media effects

Some utilities are required, i.e. water cooling, but the impact is not significant.

Operational data

No information provided.

Economics

Low additional investment and operating costs.

5.1.2 Plant initial start-up

Description

Following construction and commissioning of a major industrial unit, it is standard practice in industry to conduct a performance test of the facility. The test most often occurs within 180 days after completion of plant commissioning so that the “as built” performance of the plant is determined, this sets the baseline performance of the unit. The objectives of the performance test are typically to:

- verify the efficiency and / or capacity of the new unit, relative to either the documented guarantee or design;
- verify the in-specification production of the products, hydrogen / carbon monoxide / syngas, to either the documented guarantee or design;
- demonstrate specific operating capabilities (for example minimum load operation, action of safety devices as per design, etc.); and
- verify compliance with environmental operating permit requirements, such as emissions limits.

Preparation for the performance tests requires start-up, adjustment of sub-processes and controller tuning as well as demonstration of stable operation, check of equipment and control functionality. This frequently requires shutdowns and restarts of sub processes or of the whole unit. The final performance test can be started after completion of these activities. The duration of such preparation work varies depending on complexity and interfaces with other facilities and may take up to several weeks.

The duration of the performance test varies depending on the size and complexity of the unit, as well as the specific purpose of the test, but 24 hours is typical. During this time period, the unit will be held in defined operating modes, including a certain period of time at full load (typically 6 to 12 hours) while performance data are collected to verify the objectives as indicated above.

These data are most often averaged over the performance test period to determine the efficiency and capacity of the unit, and the calculated values are evaluated relative to those documented in the design specifications, environmental permit and / or performance guarantees.

Given that the unit needs to run at full design capacity and that the products of hydrogen and syngas plants are not materials that can be stored in significant quantity by producers or by consumers, venting or flaring of products may be required. Consequently, the performance test is structured and optimised to ensure minimum wastage of product and to minimise emissions from venting and flaring.

Achieved environmental benefits

Verification of unit's performance including environmental operating permit requirements and at the same time minimising emissions and loss of product.

Cross media effects

During performance testing and verification, plant may be operating close to permitted environmental limits.

Operational data

None published.

Applicability

Applicable to all new and retrofitted or expanded large hydrogen / syngas units.

Economics

Performance test periods are optimised to minimise wastage of feed, utilities and product that cannot be stored or beneficially used.