



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 Doc183 is withdrawn.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of Hydrogen, the Co-Production of Hydrogen, Carbon Monoxide and their Mixtures by Steam Methane Reforming* [1].¹ (withdrawn).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.

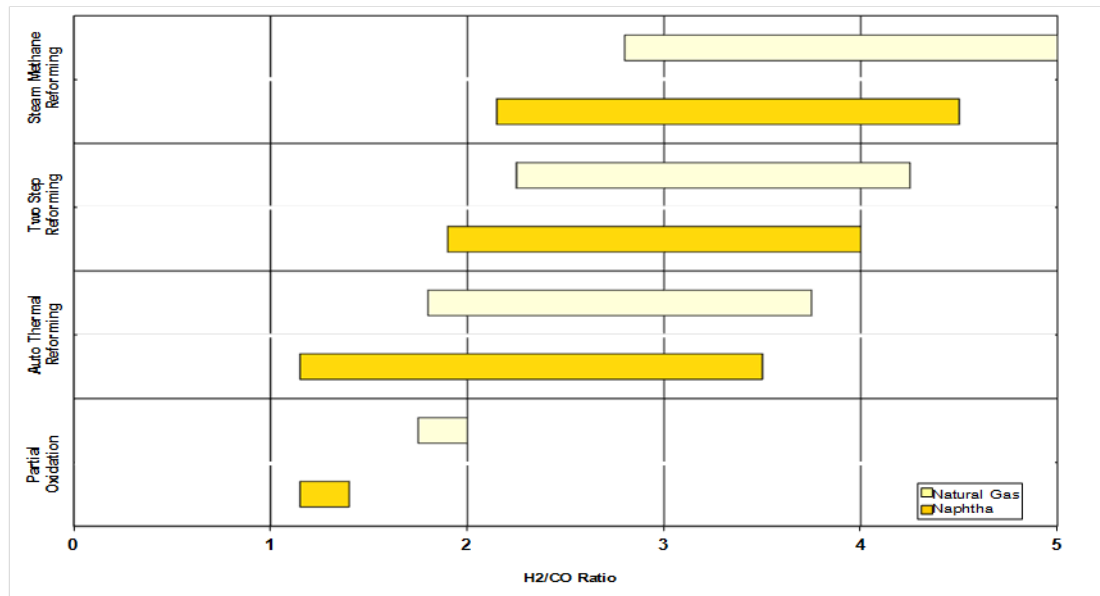


Figure 1 – H_2/CO split for HyCO process technologies [5]

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

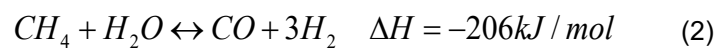
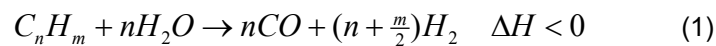
- membranes.

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 H₂/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, H₂ 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.

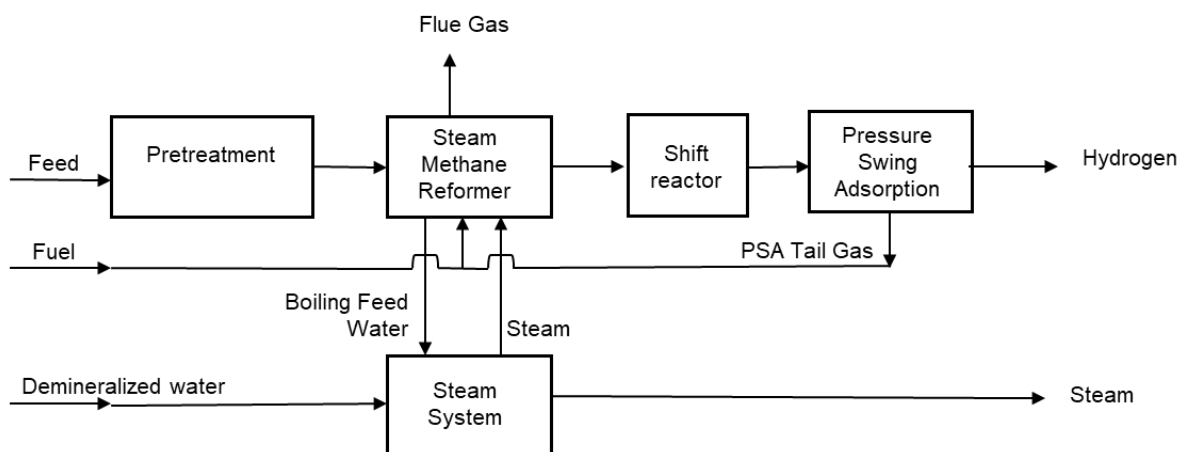


Figure 2 – Production of pure hydrogen and steam

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 H₂/CO split, carbon dioxide may be fed back to the reformer as feedstock to increase carbon monoxide yield.

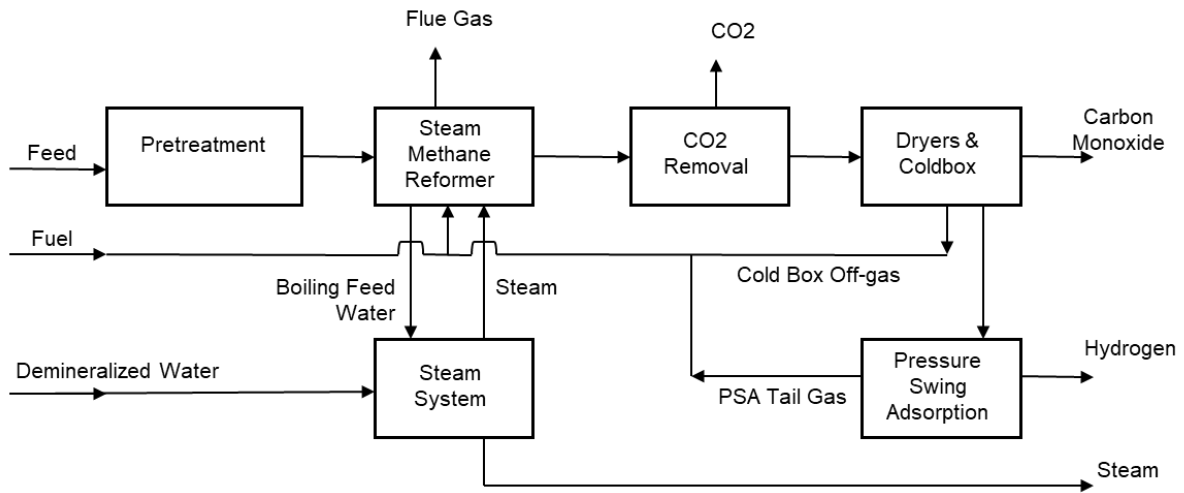


Figure 3 – Co-production of hydrogen, carbon monoxide and steam

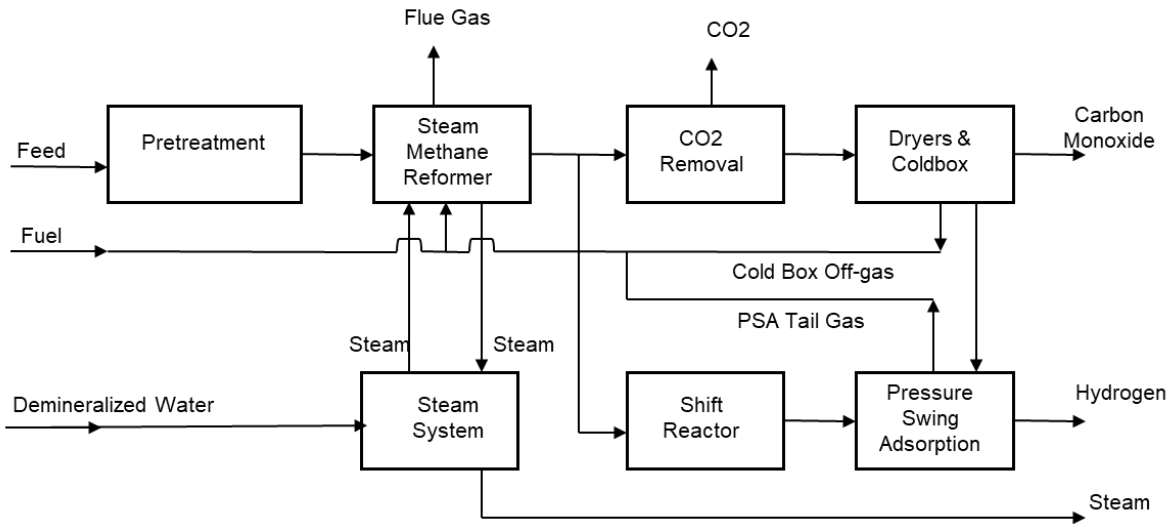


Figure 4 – Co-production of hydrogen, carbon monoxide and steam along with a shift reactor

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.

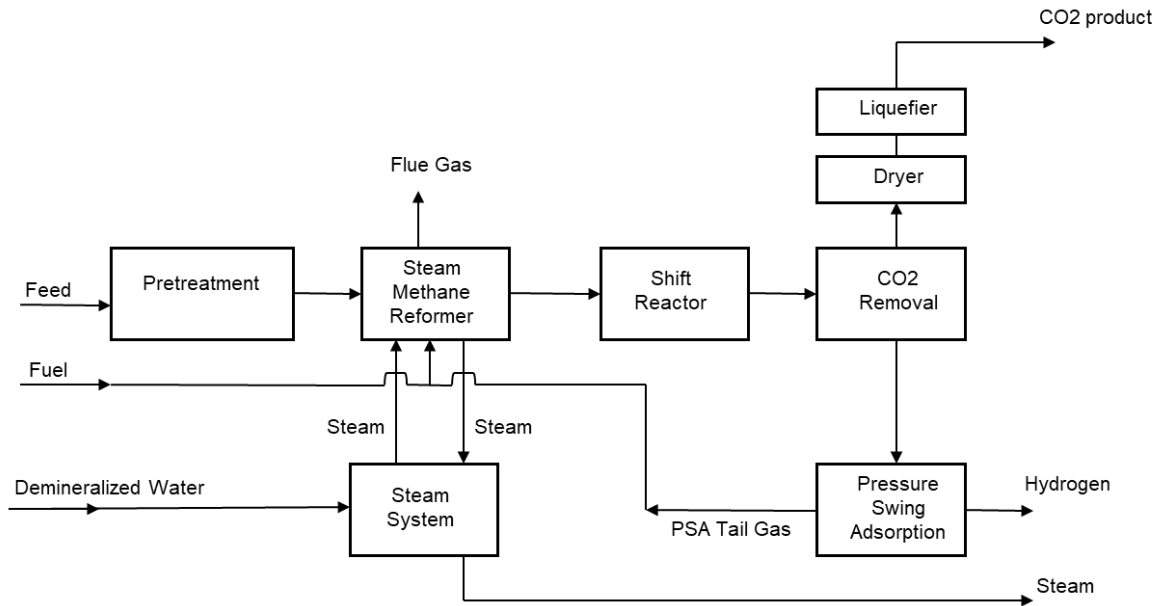


Figure 5 – Co-production of hydrogen and steam with complementary carbon dioxide production

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.

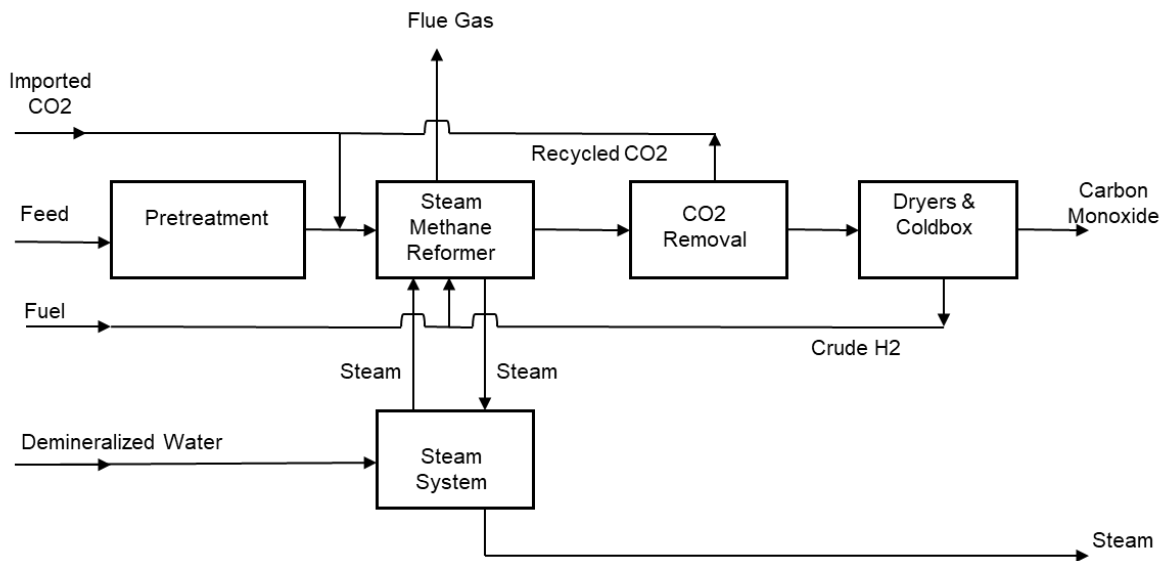


Figure 6 – Production of carbon monoxide and steam

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.

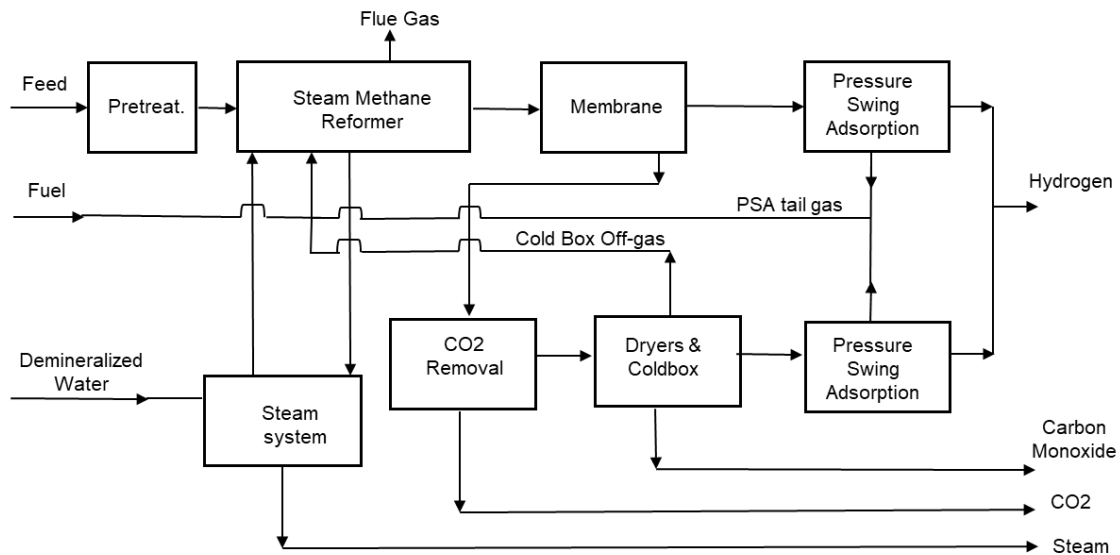


Figure 7 – Use of membrane in hydrogen and carbon monoxide production

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.

Driving force for implementation

Verify design and comply with environmental permit conditions.

Example units

Refer to plant performance testing standard [12].

5.1.3 Pre-reforming

Description

A pre-reformer installed prior to the primary reformer, in combination with a suitable steam saving project, reduces energy consumption and reduces marginally the NO_x emissions. Pre-reforming takes place through an adiabatically operated catalyst bed, before the primary reformer. The primary reforming duty is reduced as less firing is needed (less NO_x emissions) allowing, at the same time, a lower steam / carbon (S/C) ratio (energy saving) to be achieved.

Achieved environmental benefits

- Up to 5 – 10 % heat load reduction (reduced energy consumption).
- Reduced emissions to air.

Cross-media effects

Compared to steam reforming process, without pre-reforming the following cross-media effects shall be taken into account:

- less export steam generation, which counterbalances the heat load reduction above;
- higher investment costs (additional equipment as pre-reformer, pre-reformer feed superheater in waste heat recovery unit (WHRU);
- higher operating costs (additional catalyst to be exchanged); and
- higher catalyst waste generation rate since pre-reformer catalysts is highly reactive and needs to be exchanged more often as compared to reformer catalyst.

Operational Data

No information provided.

Applicability

This is an integrated technique applicable in new and existing conventional steam reforming plants.

Introducing pre-reforming into an existing plant generally would be a retrofit with significant plant changes.

Economics

Additional investment and operating costs.

Driving Force for Implementation

Conversion of steam savings to fuel gas savings.

Reference Literature

BREF for Refining Mineral Oil and Gas [3].

5.2 Energy efficient techniques

5.2.1 Energy efficiency management system techniques

Description

HyCO plants should take advantage of co-production synergies wherever technically and economically feasible. This would lead to integration into energy management systems of nearby sites. Available energy sources (refinery gas, steam, heat, power, etc.) from nearby sites can also be used and exported back so as to be integrated in facility operations.

An efficiency evaluation at the plant design stage should be used to identify these opportunities to input into the design process, referring to the range of energy efficiency techniques as described in BREF on Refining of Mineral Oil and Gas (Section 4.10.1.2, Heat integration / recovery techniques, and Section 4.10.1.2.2.1, Steam management and reduction of steam consumption) [3]. The main techniques are optimised waste heat recovery to minimise fuel consumption, and integration into the energy system of the nearby site. In addition, energy efficiency can be improved by either optimising the conversion of the feed and / or the combustion efficiency.

Plant control and the maintenance system should be designed to ensure that energy is used as efficiently as possible, with the constraints of the safe and reliable operation of the plant and the design energy import and export requirements. Further guidelines on energy management system techniques can be found in the BREF on Energy Efficiency [13].

In addition, several techniques can be used to integrate the energy usage and to improve overall plant efficiency by energy optimisation. For example:

- optimise heat integration by usage of cold streams from the cold box for pre-cooling of warm streams;
- use of syngas or low-pressure steam to regenerate carbon dioxide loaded MDEA in the carbon dioxide removal system;
- recycle of coldbox off-gas, PSA-purge gas, membrane residual gas as fuel;
- better feedstock usage by carbon dioxide recycle (for CO-plants only); and
- use of syngas to produce extra steam.

Achieved environmental benefits

These measures increase energy efficiency of the HyCO plant and any associated facility, thus reducing greenhouse gas emissions (overall balance).

Cross-media effects

None.

Operational data

Fuel requirement values indicated in Table 1 are those associated with hydrogen production strictly. They refer to large size equipment, large meaning 50 000 Nm³/h of hydrogen or more. Those recent processes produce 3000 – 3600 Nm³ of hydrogen per tonne of feedstock.

Achieving values as low as 20 000 MJ/T hydrogen requires not only to use BAT such as efficient heat recovery from the flue gases by preheating process feed, steam superheating and combustion air preheat, but also to use PSA separation process in order to recover energy contained in by-products,

mainly carbon monoxide, fed back to burners. Such recovery of heat and fuel energy can achieve up to 80-90% of the required energy for steam reforming to produce hydrogen, depending mainly on co-production requirements.

The steam reformer has to supply, by burning fuel, a large amount of heat at high temperature for the steam reforming reaction. Global fuel consumption of a unit includes that for hydrogen production plus that associated with steam export to nearby installation. As more and more steam is produced and exported, total energy requirements can be higher.

Values of electricity requirement do not include product compression. Neither is cooling for such compressors included in the values presented for water cooling utility.

The values in Table 1 may be compared to those published elsewhere such as Sema and Sofres, where values ranging from 35 000 up to 80 000 MJ/T hydrogen are mentioned [14]. Such values are typical of installations where steam reforming is followed by a shift unit, combining carbon monoxide and steam, to produce more hydrogen. Hence, tail gases were not recovered and fed back to burners since their energy content has been reduced. Poor heat recovery in the convective section of the reformer results that a large amount of heat is lost in the flue gas.

Recently designed large size steam reforming units, including BAT on energy efficiency, can achieve the values in Table 1.

Table 1 – Requirements for steam reforming based on recent large size equipment including BAT on energy efficiency

Fuel (MJ/T H ₂)	Electricity (kWh/T H ₂)	Steam produced (kg/T H ₂)	Cooling water (m ³ /T H ₂ , ΔT=10 °C)
8750 – 22 500 (In case of high steam production, fuel values can increase to 44 000 MJ/T H ₂)	200 – 400	2000 – 14 000	25 – 100

The appendix shows simplified process modelling, which illustrates the variety of hydrogen production parameters and their relative environmental impact.

Driving force for implementation

Increasing energy efficiency and thus reducing greenhouse gas emissions.

5.2.2 Minimal steam / carbon ratio and associated measurement

Description

One essential design technique for improving the global thermal balance is the optimisation of the molar ratio of steam to hydrocarbon feedstock (S/C) entering the reformer. As described in Section 4, steam reacts with hydrocarbons to produce hydrogen. However, not all of the steam is depleted as the chemical equilibrium of reactions 2 and 3 defines the composition of the wet reformed gas. If the steam flow is higher than optimal, as defined by the H₂/CO products ratio, the unreacted portion will effectively be heated up only to be cooled again with the steam methane reformer. As a result, too high a S/C ratio reduces the thermal efficiency of the plant. Too low a S/C ratio increases the quantity of unreacted methane. Thus, reducing the hydrogen and carbon monoxide output and increases the risk of by-product formation and increased pressure drop in the HT shift reactor. and the reformer [15]. In order to compensate the quantity of unreacted methane, the reformer outlet temperature is raised [16]. In operation, the flow measurements of steam and hydrocarbon are used to control the S/C ratio.

The optimum operating range of S/C ratio depends upon the customer requirements for H₂/CO product split and co-produced steam. For example, in cases where exported steam is considered a valuable

product, a reduction of the S/C ratio allows the system to use less steam and produce very efficiently a larger quantity of export steam, thus improving the thermal efficiency.

Achieved environmental benefits

The reduction of the S/C ratio results in an improved thermal efficiency by reducing the consumption of fuel (firing heat), cooling water (amount of low temperature heat) and electricity (fans power). While a number of references provide indicative numerical results, the relative and absolute values depend strongly on the parameters above [16].

Cross-media effects

The optimum adjustment of the S/C ratio in combination with the reformer outlet temperature has an effect on NO_x formation. The concentration of some by-products (for example methanol, acetic acid) will increase.

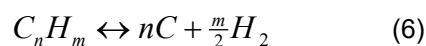
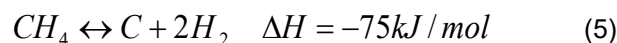
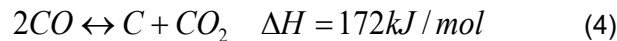
Operational data

The limitation on the S/C ratio is driven by the steam reformer catalyst and depends on feed type, selected parameters, reformer configuration, CO shift selection, etc. Typical values range from 2 to 4 with a minimum down to 1.5. When there is no shift present, the S/C value may be reduced down to 1.5 where the plant is used for syngas generation only, as higher S/C ratios around 3 are required for hydrogen production.

Applicability

The S/C ratio cannot be reduced indefinitely to a stoichiometric level due to risks within the SMR reactor.

In the SMR, there is the risk of carbon deposition (coking) by the three equations below [15]:



Such carbon deposition leads to breakdown of the catalyst, further carbon deposits, blockage of the tubes and the development of hot spots. To prevent such a scenario, the S/C ratio shall be maintained sufficiently high. At a given temperature, the risk of carbon deposition is greater for heavier hydrocarbon feedstock, and so the critical S/C ratio is higher in this case [15]. The maximum reformer outlet temperature is limited by mechanical constraints of the reformer tube and / or outlet system at high temperature. The S/C ratio and reformer outlet temperature shall be controlled to ensure safe and reliable operation.

Economics

For a given quantity of CO or syngas product, reducing the S/C ratio may reduce both operating and investment cost. While case studies have been reported, the relative and absolute cost improvements depend on production capacity, and the valuation of co-products (for example steam) amongst other variables [16].

Driving force for implementation

The minimum S/C is a point of continual technological improvement because it results in some case in product and cost efficiencies. However, on a plant-by-plant basis the S/C shall be optimised depending on the required H₂/CO split and steam valorisation.

Example plants

Many plants in Europe use this technique, although the final S/C ratio depends on all the factors mentioned above.

5.2.3 Air pre-heat

Description

The application of air preheating in steam methane reformers (SMR) with forced air draft for hydrogen production as described as a BAT option for increasing furnace efficiency in Chapter 4.10.3.1 of the BREF on Refining Mineral Oil and Gas shall be evaluated carefully with regard to the resulting increased NO_x production [3].

Usually, steam is produced in the waste heat recovery unit (WHRU) of an SMR, which contributes to the total steam production for the nearby site and increases also significantly the energy efficiency of the SMR furnace. Thus, air preheating may be replaced by optimised steam production in the WHRU as an adequate alternative, when the steam production is already required at a specific site. Such selection depends strongly on the demand for export steam and its valorisation.

Achieved environmental benefits

Increasing energy efficiency and thus reducing greenhouse gas emissions (overall balance).

Cross-media effects

Increased combustion air temperatures increase NO_x emissions from the combustion of fuel gases in the furnace. Optimised steam production with export to refinery consumers has to be evaluated carefully as an alternative without increased NO_x emissions. Reference is also made to the BREF on Large Combustion Plants §3.2.2.3.4, §10.4.1.2 or §10.8.3 and the BREF on Energy Efficiency Chapter §3.1.1 [17, 13].

Operational data

Achievable overall energy efficiency and thus reduction of greenhouse gas emissions is depending on the specific project situation.

The positive effect of air preheating on carbon dioxide emissions shall be balanced against the negative effect on NO_x emissions. Reference is made to Chapter 3.1.1.1 of the BREF on Energy Efficiency [13].

Waste heat recovery by optimised steam production shall also be considered as adequate alternative, if steam production is required.

Applicability

Application is possible for new installations. Applicability of installation of air preheating for existing installations requires detailed case specific evaluation with regard to existing flue gas duct geometry and required operating conditions. Reference is made to the BREF on Energy Efficiency Chapter 3.1.1.1 [13]. This technique is not applicable for natural draft reformers.

Economics

Investment as well as operational costs and potential savings for air preheating as well as for optimised steam production depend on the specific project situation and shall be evaluated carefully.

Driving force for implementation

Increasing energy efficiency and thus reducing greenhouse gas emissions.

Example plants

There are many examples of installed SMRs including air preheating.

5.3 Abatement of air emissions

The main emissions to air from a HyCO plant are combustion flue gases from the process and potentially include:

- carbon dioxide;
- NO_x;
- carbon monoxide; and
- SO_x.

The main emission is carbon dioxide, which is not covered in the IED but by EU emissions trading scheme (ETS).

Hydrogen as well as HYCO plants have minimal SO_x emissions.

The steam methane reforming process requires the desulphurisation of the feed so as to prevent catalyst poisoning, this also protects from unexpected spikes in sulphur in the fuel and flue gas. As a result, the tail gas from the PSA and from the coldbox, if present for carbon monoxide separation, is free of sulphur. As this recovered gas forms a significant amount of the fuel, SO_x emissions are correspondingly reduced. This also depends on the sulphur content of the supplementary fuel.

5.3.1 NO_x abatement

Existing best available technique for the abatement of NO_x emissions are:

- a) Use a relatively small quantity of excess air.

Steam methane reforming typically requires 5-10% excess air with the minimum value being limited by safety considerations and CO emissions (cross-media effect). Further details on this technique can be found in the BREF on Large Combustion Plants [17].

- b) Use of low-NO_x burners to burn PSA tail gas and other gaseous fuels.

In order to provide stable operation of the SMR, low NO_x or ultra-low NO_x burner design should be selected carefully with regard to operating conditions and burner turn-down requirements for the specific operating cases.

- c) End-of the pipe treatments are also to be considered.

They are of two types: Selective catalytic reduction with the aid of a catalyst and selective non catalytic reduction by means of injecting into the flue gas ammonia or urea.

5.3.1.1 Low NO_x burners

Low NO_x burners, either air-staged or fuel-staged, have the aim of reducing peak temperatures, reducing the oxygen concentration in the primary combustion zone, and reducing the residence time at high temperatures, thereby decreasing thermally formed NO_x.

When using fuel staging, a primary combustion zone is created with a little amount of fuel and all the combustion air for the desired heat released. The fuel lean zone in the burner is relatively cold, generating small amounts of NO_x emissions. In the secondary combustion zone, the remaining fuel gas is added to the combustion products and the remaining combustion air from the first zone to complete combustion.

Air staging uses a similar concept, but instead of staging the fuel gas, air is added in delayed steps to the combustion zone. A primary combustion zone is first established, where all of the fuel gas is mixed

with a fraction of the combustion air. This generates a very fuel rich zone, which also limits the flame temperature due to oxygen depletion. The remaining air is then added downstream of the primary zone to complete the combustion.

Applicability

The use of low-NO_x burners as a process-integrated measure provides a significant reduction of NO_x emissions compared with conventional burner designs based upon the same fuel.

Driving Force for Implementation

Reduction of NO_x emissions.

Operational Data

Applicable low-NO_x or ultra-low NO_x burner type and achievable emission levels depend on the specific situation. The following constraints should be considered:

- SMR reaction requires high reforming temperatures (around 750-1000 °C);
- specific fire box geometry (long heated tubes, box dimensions, etc.);
- burner to burner spacing;
- burner to tube spacing;
- plant and burner turndown rate;
- fuel gas composition flexibility;
- extent of air preheating;
- even air / fuel mixing to prevent carbon monoxide and unburned hydrocarbon emissions;
- composition range of available supplementary fuel gas; and
- fuel gas pressure at burner.

Utilisation of tail gas with high hydrogen content has the effect of increasing NO_x formation.

Due to these aspects, NO_x emission levels achievable in an SMR are higher than those of boilers and other fired heaters.

Increased NO_x emission values for HyCO plants and those plant that co-produce CO₂ compared to pure hydrogen plants are due to higher firing temperatures as needed for the process and use of different fuel gas compositions, which furthermore increase the flame temperature because of:

- less inert gas (lower CO₂ content in PSA purge gas); and
- higher hydrogen content in the PSA purge gas fed back to burners.

Achieved environmental benefits

Typical NO_x emission values (calculated as NO₂ in dry flue gas with 3 vol-% O₂) when the fuel does not include significant CO₂ content are shown in Table 2.

Table 2 – NOx emission values upon firing low NOx burners

<i>Low NOx burners</i>	<i>Without air preheat</i>	<i>With air preheating:</i>
Hydrogen SMR plants	100 to 140 mg/Nm ³ (50-70 ppmv)	up to 200 mg/Nm ³ (100 ppmv)
Hydrogen & Carbon Monoxide (HyCO) SMR plants	200 to 240 mg/Nm ³ (100-120 ppmv)	Up to 300 mg/Nm ³ (150 ppmv)

The values indicated in the Table 2 are to be understood as yearly averaged values, not as spot measurements, nor as maximum values not to be exceeded in case of continuous measurements monitoring.

Cross-media effects

No cross-media effects, as there are no additional environmental impacts.

The application of low-NOx burners does not cause additional energy or other utility consumption.

Example plants

There are many examples of SMRs using PSA tail gas in combination with low-NOx burners.

5.3.1.2 Ultra-low NOx burners

Ultra-low NOx burners include the addition of other concepts, such as internal or external flue gas recirculation, on top of the low NOx burner air or fuel staging.

Internal recirculation means that flue gases in hydrogen reformer units are recirculated inside the furnace, driven by fuel pressure and burner design. External recirculation uses additional fans to recirculate the furnace flue gases.

Applicability

Ultra-low NOx burners are most suitable for gas fired based SMRs. Application is straightforward for new installations. Applicability of retrofitting ultra-low NOx burners for existing installations requires detailed evaluation with regard to existing fire box geometry and required operating conditions.

Reference is made to Chapter 4.10.4.1 of the BREF on Refining of Mineral Oil and Gas [3].

SMR specific aspects to be considered for burner type selection have been described in the section on operational data for low NOx burners. They also apply to ultra-low NOx burners.

Driving Force for Implementation

Reduction of NOx emissions.

Achieved environmental benefits

Typical NOx emission values (calculated as NO₂ in dry flue gas with 3 vol-% O₂) when the fuel does not include significant CO₂ content are shown in Table 3.

Table 3 – NOx emission values upon firing ultra-low NOx burners

<i>Ultra-low NOx burners</i>	<i>Without air preheat</i>	<i>With air preheating</i>
Hydrogen SMR plants	80 to 120 mg/Nm ³ (40-60 ppmv)	100 to 150 mg/Nm ³ (50 - 75 ppmv)
Hydrogen & Carbon Monoxide (HyCO) SMR plants	120 to 150 mg/Nm ³ (60-75 ppmv).	Up to 200 mg/Nm ³ (100 ppmv)

The values indicated in Table 3 are to be understood as yearly averaged values, not as spot measurements, nor as maximum values not to be exceeded in case of continuous measurements monitoring.

For achievement of even lower NOx figures, techniques such as selective catalytic reduction (SCR), see 5.3.1.3 and selective non-catalytic reduction (SNCR), see 5.3.1.4, should be considered.

Cross-media effects

For increasing efficiency, temperature of the air pre-heat may significantly increase above 350 °C. In this case the NOx concentrations may rise up to 300 mg/Nm³.

Economics

The investment cost of low NOx burners is typically in the range of 130 to 180% of that of conventional low NOx burners. This higher initial investment can still pay off compared to a SNCR solution since it does not require continuous supply of consumables like urea.

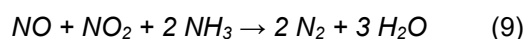
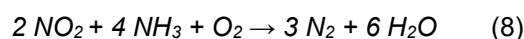
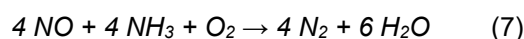
Reference Literature

BREF on Large Combustion Plants [17].

5.3.1.3 Selective catalytic reduction

Description

Selective catalytic reduction is a means of converting nitrogen oxides (NOx) with the aid of a catalyst into diatomic nitrogen (N₂) and water (H₂O). In SCR systems, ammonia vapour (or vaporised ammonia solution) is used as the reducing agent and is injected into the flue gas. NOx emission reductions over 70-95% are achieved [3]. The optimum flue gas temperature for the SCR system is usually between 300 °C and 400 °C.



The efficiency of SCR process reactions (reagent stoichiometry and utilisation nearly 1.0) allows very close and effective reagent injection-control based on feedback of measured NOx concentrations in the flue gas at the economiser or combustion air preheater outlet. The temperature of the flue gas in the SCR reactor is controlled if required, for example by mixing the flue gas exiting the economiser with the flue gas from the economiser bypass or reinjecting into the stack. The ammonia injection grid is located in the ductwork leading to the SCR catalyst, far enough upstream to ensure optimum gas and reagent distribution across the catalyst cross-section.

The catalysts can have different compositions: based on titanium oxide, zeolite, iron oxide or activated carbon. Most catalysts in use in SMR plants consist of vanadium (active catalyst) and titanium (used to disperse and support the vanadium) mixture. However, the final catalyst composition can consist of many active metals and support materials to meet specific requirements in each SCR installation. Catalyst geometry may typically be a flat plate or honeycomb. A moving bed is used for granular activated carbon. Experience shows that plate types generally have a higher resistance to deposition and erosion than honeycombs. In this case, catalytic converters may be used inside an air preheater.

Achieved environmental benefits

Commercial selective catalytic reduction systems have been shown to reduce NO_x by 70-95% [3].

Cross-media effects

Compared to steam reforming processes without SCR, the following cross-media effects shall be taken into account:

- additional reducing agent such as ammonia required: ammonia slip leads to ammonia emissions; and
- higher catalyst waste generation rate (typically once every 3-4 years), timed around customer outages.

Operational data

No information provided.

Applicability

This is an integrated technique applicable in new and existing conventional steam reforming plants. For existing plants this is only applicable if there is room to install a fan to accommodate the extra pressure drop.

Economics

Compared to a steam reforming process without SCR, additional investment and operating shall be taken into account:

- higher investment costs (additional SCR equipment); and
- higher operating costs (additional reducing agent such as ammonia required, and additional power is required due to increased required pressure drop of the induced draft flue gas fan and potentially required auxiliary blower for dosing).

Driving force for implementation

Reduction in NO_x emissions.

Example plants

There are globally many examples of SMRs using SCR.

Reference literature

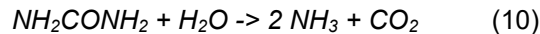
Steam: Its generation and use [20].

5.3.1.4 Selective non-catalytic reduction

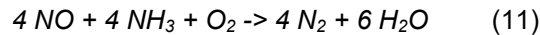
Description

The process involves injecting either ammonia or urea into the flue gas at a location where the flue gas is between 760 and 1093 °C (1400 and 2000 °F) to react with the nitrogen oxides formed in the combustion process. The resulting product of the chemical redox reaction is elemental nitrogen (N₂), carbon dioxide (CO₂) in case of urea as reduction agent, and water (H₂O).

Urea (NH₂CONH₂) is easier to handle and store than the more dangerous ammonia (NH₃). In the process, it reacts like ammonia after conversion:



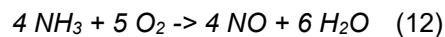
The reduction happens according to (simplified):



The reaction mechanism itself involves NH₂ radicals that attach to NO and then decompose.

The reaction requires a certain temperature range to be effective, typically 760 to 1093 °C (1400 to 1999 °F), otherwise the NO and the ammonia don't react to form the desired products. Ammonia that hasn't reacted is called ammonia slip and is undesirable, as this would lead to continuous ammonia emissions. Besides that, the ammonia can react with other combustion species, such as sulphur trioxide (SO₃), to form ammonium salts [2].

At temperatures above 1093 °C ammonia decomposes:



In that case NO is formed instead of N₂. Thus, the reaction needs a specific temperature window to be efficient. The reaction also needs sufficient reaction time in that temperature window.

A further complication is mixing. Generally, more NO will form in the centre and less near the walls, as the walls are cooler than the centre. Thus, optimally more ammonia must find its way to the centre and less near the walls, otherwise NO in the centre meets insufficient ammonia for reduction and excess ammonia near the walls slips through.

Though in theory selective non-catalytic reduction can achieve the same efficiency of about 90% as selective catalytic reduction (SCR), these practical constraints of temperature, residence time, and mixing always leads to a lower conversion in practice. However, selective non-catalytic reduction has an economical advantage over selective catalytic reduction, as the cost of the catalyst is saved.

Achieved environmental benefits

- Reduced NO_x emissions.

Cross-media effects

Additional reducing agent such as ammonia is required. Ammonia slip leads to ammonia emissions.

Operational Data

No information provided.

Applicability

This is an integrated technique applicable in new and existing conventional steam reforming plants. Despite a high retrofit complexity, SNCR are easier to retrofit than SCR.

Economics

Compared to a steam reforming process without SNCR, additional investment and operating costs shall be taken into account, including:

- higher investment costs (additional SNCR equipment); and
- higher operating costs (additional reducing agent such as ammonia required).

Driving force for implementation

Reduction in NO_x emissions.

Example plants

There are some examples of SMRs using SNCR.

Reference literature

Kinetics of the gas-phase reaction between nitric oxide, ammonia and oxygen [22].

Steam: Its generation and use [20].

5.3.2 Oxygen and / or carbon monoxide monitoring

Description

The monitoring of oxygen and / or carbon monoxide content in the steam methane reformer's flue gas can be used to limit the emission of carbon monoxide and unburned hydrocarbons. This is achieved when the appropriate fuel / air ratio is maintained. The fuel gas quantity is fixed by the required duty in the reformer. The combustion air is typically controlled to get 2% excess oxygen in the flue gas corresponding to approximately 10% excess air flow. Thus, by monitoring the excess oxygen content in the flue gas complete combustion is maintained.

As incomplete combustion results in an increased carbon monoxide content in the flue gas, also monitoring the carbon monoxide concentration in the flue gas can be applied for combustion control. In the event that the plant has natural draft air, the operator manually adjusts the quantity of excess air.

Achieved environmental benefits

The monitoring of oxygen and / or carbon monoxide content in the steam methane reformer's flue gas can be used to control combustion efficiency and thus limit the emission of carbon monoxide and unburned hydrocarbons.

Cross-media effects

None.

Operational data

To ensure good combustion efficiency, approximately 10% excess air is used to maintain approximately 2% oxygen in the flue gas.

Applicability

All HyCO plants.

Economics

Fuel consumption is optimised.

Driving force for implementation

Continuous oxygen monitoring is common industrial practice to control the combustion efficiency.

5.3.3 Fugitive emissions

Fugitive emissions are emissions from equipment that cannot reasonably pass through a stack, chimney, or vent or other functionally equivalent opening. They are mostly due to leaks from pressurised equipment that are sometimes too small to detect and repair and are not due to loss of containment from an unexpected sealing device failure.

Fugitive emissions are not considered to be significant for hydrogen plants, but the following best practices may be applied.

Reference is made to EIGA Doc 215, *HyCO Plant Gas Leak Detection and Response Practices*, Section 7.5 (environmental considerations) regarding fugitive emissions monitoring and section 8 (operational and design consideration to avoid potential leaks) [23].

Fugitive emissions can be reduced by the detection and subsequent repair or replacement of leaking components by implementing a leak detection and repair programme or using certified technical tight equipment [24].

Achieved environmental benefits

- Prevention and reduction of fugitive emissions.
- Increase safety to personnel equipment and facilities.
- Reduced emissions to atmosphere.

Cross media effect

None.

Applicability

All HyCO plants.

Driving force for implementation

Reduction in material losses, reduction of hazardous or toxic emissions for the health and safety of personnel.

5.3.4 Carbon monoxide leak prevention

Description

Carbon monoxide is flammable in air over a very wide range (12.5% – 74%), it is toxic and, as it has almost the same density as air, it will not diffuse readily into the atmosphere. It is especially dangerous because it is colourless, odourless, and possesses no properties which might warn of its presence.

For these reasons, leak prevention together with appropriate installation and usage of leak detection devices and the use of safety personal protective equipment (PPE) are particularly important on a HyCO plant.

In the coldbox, where the carbon monoxide is purified into product, best practice for carbon monoxide leak prevention is to reduce the use of flanged joints as far as possible and instead use welded pipe connections. Furthermore, bellows or diaphragm type valves should be used.

Generally flanged connections should be minimised and only used to connect equipment that may have to be removed for maintenance, for example carbon monoxide compressor.

On the carbon monoxide compressor itself, a mechanical sealing system to separate the process from the gear side shall ensure the possibility of carbon monoxide leakage such that it is eliminated to the extent possible. On reciprocating compressors, a multiple stage mechanical sealing system is common, in which the space between the outer seals is continually purged with nitrogen and maintained at a pressure higher than the space between the inner seals, which is exhausted to flare. Pressure alarms shall be installed on the exit of this inner seal purge chamber to warn of any change in condition to the integrity of the seals.

If there is liquid carbon monoxide storage in the plant, it shall be contained in a double shell facility, for example a dedicated tank shall be double walled and vacuum insulated, with a pressure transmitter monitoring the vacuum space to check for loss of vacuum indicating potential leaks. Physical protection of the tank is also important to protect against damage by site traffic for example bollards / crash barriers in the tank vicinity, etc. Alternatively, the liquid carbon monoxide can be also stored within the coldbox in a single walled vessel since the coldbox shell itself represents the second barrier.

Plant operating and maintenance procedures should address measures how to prevent or mitigate leakage of toxic or flammable gas.

In areas where a toxic or flammable gas release is possible, personal portable monitors should be used.

Achieved environmental benefits

- Increased safety to personnel, equipment and facilities.
- Reduced emissions to the atmosphere.

Cross-media effects

None.

Operational data

No information provided.

Applicability

All HyCO plants.

Economics

None available.

Driving force for implementation

Carbon monoxide leakage can lead to a major hazard to personnel, equipment or facilities.

5.3.5 Integrated monitoring scheme rationalisation

Description

Installation of adequate sample ports in the flue gas stack of gas-fired methane-based steam reformers (SMR) for hydrogen production is considered to be BAT with regard to emission monitoring.

As the SMR operation is a very stable process and as stated previously, due to the low sulphur gas firing only NO_x and carbon monoxide shall be considered as relevant emission components.

Occasional measurements for compliance verification is recommended for SMR's not subject to Directive 2010/75/EU on the limitation of emissions of certain pollutants into the air from large combustion plants [2].

Installing continuous monitoring on existing installations is not as straightforward as it may seem at first glance. The emission points need to be adapted, monitors need to be installed and, depending on the member state, be subject to accreditation processes, so retrofits may not be BAT.

EN 15259, *Air quality. Measurement of stationary source emissions. Requirements for measurement sections and sites and for the measurement objective, plan and report*, regulates detailed design aspects for the installation of sample ports and measurement planning [25]. Main aspects are sufficient number of sample ports, adequate sample port location and accessibility. With respect to accessibility, mobile scaffolding may be considered with regard to the low measurement frequency required.

Achieved environmental benefits

This introduces the possibility of direct measurement for verification of compliance with emission limit values or for other reasons, for example periodic environmental reporting.

Cross-media effects

None.

Operational data

For gaseous fuel firing facilities, relevant emission components to be considered for design of sampling ports are NO_x and carbon monoxide. Also, oxygen measurement (for calculation of emissions to reference conditions) shall be considered.

In the event that flue gas flow monitoring is required, the flue gas flow can be calculated on the basis of the fuel flow measurement, its heating value and stoichiometric air demand.

The PSA tail gas usually applied as fuel gas is sulphur free and also other supplementary gaseous fuels applied are usually of low sulphur type, thus measurement of SO_x normally does not need to be considered. Due to clean gas firing and related low dust emissions, also specific precautions for sample ports regarding particulate measurement (isokinetic sampling) normally do not need to be considered.

Applicability

Application is possible for new installations.

Applicability for existing installations requires case specific evaluation with regard to existing duct geometry.

As the processes are stable and controlled via other process parameters, a continuous monitoring is unlikely to improve the environmental performance. Small steam reformers should be monitored periodically on an annual basis. According to the threshold as in BREF on Refining of Mineral Oil and Gas continuous monitoring is required only for to large units greater than 50 MW_{th} input [3].

Economics

The cost of sampling installations and analysers may be significant depending on the required frequency and local authorities' requirements.

Driving force for implementation

Ensure possibility of direct measurement for verification of compliance with emission limit values or for other reasons, for example periodic environmental reporting.

Example plants

There are many examples of SMRs using occasional direct emission measurements for compliance verification.

Reference literature

JRC Reference Report on Monitoring of Emissions to Air and Water from IED Installations [26].

5.3.6 Cryogenic gas disposal system in carbon monoxide production units

Description

It is necessary to connect the cryogenic hydrocarbon system to a vaporisation and blow down system connected to flare gas system so that cryogenic hydrocarbons can be safely disposed of whenever a cold box stop is required by production planning, maintenance or need to empty the cold box. This is often a separate dedicated line to the hot flare. The hot flare shall be equipped with a pilot flame to ensure full conversion of carbon monoxide and CH₄ into carbon dioxide.

Usually the release flow rate may be kept at a low value, but for the full flow case, the drain connecting the cold box to the flare should be equipped with an intermediate buffer tank that stores the liquid inventory and allows for progressive vaporisation at a low rate when compared with flows from other process units. For example, vessels equipped with a steam heater are used to ensure full vaporisation of the cryogenic liquid.

Achieved environmental benefits

Avoidance of release to the atmosphere of large amounts of vaporising carbon monoxide (toxic).

Cross-media effects

Keeping the pilot flame of the flare continuous burning represents a non-recovered heat release, but the burning rate is negligible. From a safety perspective this is unavoidable.

Applicability

To all processes including a cold box as the carbon monoxide – hydrogen separation device.

Economics

Adequate sizing of the warming-up device is required to avoid over-cost, but conservative evaluation of the vaporisation rate is a key safety issue for sufficient vaporisation and combustion.

5.3.7 Generalised noise abatement methodology

Description

A noise evaluation for the plant should be completed at the design stage and a noise management plan completed as appropriate to the local environment for example where a noise nuisance at sensitive receptors is expected. A methodology such as UK Environment Agency *Horizontal Guidance Note IPPC H3 Part 2* or the attachment of the German TA-Lärm could be used to evaluate the potential for noise impact on local receptors on and off site [27, 28].

The BREF on Refining of Mineral Oil and Gas (chapter 5.1.9) refers to the 'bubble concept', where total noise contributions for the whole site are evaluated to establish the most economically efficient ways of reducing noise to minimise nuisance [3]. Where necessary and practical the noise impacts of HyCO plants should be integrated into this assessment, for example depending on the location of the SMR relative to the main site.

Continuous contributors to the noise profile of HyCO plants when in operation include process equipment such as compressors, the PSA unit, the steam methane reformer and cooling towers. Non-continuous sources include start up and shutdown noise, alarm testing and venting / gas flaring.

There are a number of well-established techniques that should be evaluated to reduce the potential for noise nuisance from these sources and the hierarchy of noise control shall be implemented. Reference should be made to EIGA Doc 85, *Noise Management* for a suitable list of techniques [29].

Achieved environmental benefits

Minimisation of the nuisance potential.

5.3.8 Emissions to water

Steam methane reforming generates a number of liquid effluent streams, but these are not sufficiently unique from many other industrial processes to warrant process-specific abatement techniques [10, 30]. Instead, a wastewater management strategy may be used to prevent and control the impurities in the different wastewater streams. This section describes such a strategy before highlighting specific issues related to the blow downs from the boiler and the cooling tower.

Best available techniques are found in the BREF on *Common Waste Water and Waste Gas Treatment / Management Systems in the Chemical Sector* (CWW BREF) [31].

5.3.8.1 General wastewater management strategy

Facilities that co-produce hydrogen and carbon monoxide by steam methane reforming do not generate any particularly unconventional wastewater streams. Additionally, these facilities generally exist to serve other industrial facilities (for example refineries, acetic acids, cyanates) with liquid effluents that are more challenging to treat. Therefore, a centralised wastewater treatment (CWWT) plant often is part of such industrial facilities in order to meet applicable environmental standards. In such a scenario, the most environmentally effective and financially most viable solution is to divert the liquid effluents from the hydrogen / carbon monoxide co-production facility to the CWWT plant for final treatment and this shall be considered as BAT.

Such action, however, does not absolve the hydrogen / carbon monoxide co-production facility from action on-site. Instead, prevention techniques should be used to minimize the load on the CWWT plant. An effective strategy begins during the design stages and can be completed in three parts:

1. **Stream Identification** – The prevention of wastewater stream contamination begins with the identification of all water streams entering and leaving the facility. These streams enter the facility with varying levels of contamination, and then accumulate different quantities of contaminants throughout the facility. Addressing these streams collectively requires an understanding of the source and level of contamination for each stream. Establishment of inventories of wastewater and waste gas streams is BAT 2 in the CWW BREF [31].
2. **Stream segregation and collection** – These streams shall be maintained separate so as to prevent the needless contamination of otherwise unpolluted streams. In such a way, each stream can be addressed individually in terms of the appropriate collection technique. This is BAT 8 in the CWW BREF [31].
3. **Minimisation of stream flow and contamination** – Once each stream has been identified, segregated, and routed to the appropriate destination, attention may be given to reduce the flow and level of contamination in each stream. Such efforts usually require evaluation of possibilities for process alterations with the aim of avoiding or recycling wastewater flows or the minimisation of flow and contamination level. Also, monitoring the level of contamination in each stream and reducing the causes for its elevation within the constraints of the process may be considered. This is BAT 7 in the CWW BREF [31].

For further information, EIGA Doc 122 and the CWW BREF provide some relevant best available techniques in its sections on general environmental management, wastewater management, process-integrated measures, and wastewater collection [8, 31].

Given this strategy, for an SMR-based hydrogen / carbon monoxide co-production unit, the following types of liquid effluent streams have to be considered if within system boundary [8]:

- demineralised water production unit effluents;
- boiler blow down and other process condensates;
- cooling water blow down;
- rain / surface water;
- domestic water; and
- oily water from base plates of pumps and machinery or water treatment chemical containment.

Additional liquid effluents may have to be considered for other process plant constellations, for example application of BAT is to separate oily water and non-oily water streams, rain and surface water that requires no treatment and can potentially be reused, and the waste water that requires treatment before discharge to the environment (cooling water and boiler blow down and any domestic waste water).

5.3.9 Process condensates

The primary sources of process condensates are the carbon dioxide removal unit and the process gas dryer station.

Other process condensates which are generated in the cooling section of the reformed gas are generally recycled directly or indirectly back to the steam generation system and therefore are not considered as wastewater, this is BAT 7 from [17].

Condensates from carbon dioxide removal unit (solvent regeneration):

The carbon dioxide fraction out of the regeneration packing passes water wash trays for recovery of entrained solvent (amines) traces and leaves the solvent regeneration column. It is then cooled, and the major part of the separated condensate is recycled to the top of solvent regeneration column for amine backwash purpose, while a split stream may be given to the battery limit as an effluent to maintain the water balance. The produced condensate and consequently a possible waste water stream can contain solvent traces (amines) and dissolved carbon dioxide.

Condensates from process gas drier station:

Before entering the cold box, the water and the residual carbon dioxide content of the process gas shall be removed, usually by use of process gas adsorbers. Loaded adsorbers have to be regenerated, for example by a fraction of heated raw hydrogen from the cryogenic gas separation process. The hot regeneration gas containing the desorbed water and carbon dioxide is then cooled and the resulting condensate shall be separated. The produced condensate can contain dissolved synthesis gas traces and solvent traces out of the chemical wash (typically amines). If possible, these should be recycled back to the coldbox flash-gas and eventually to the reformer.

5.3.10 Boiler blowdown

Boiler blowdown is the method generally used to divert soluble contaminants accumulated in the boiler water to avoid scaling and corrosion. As in other industrial plants, it presents a significant effluent stream in an SMR facility [32]. Corrosion is one of the main causes for compromised boiler reliability and safety while scale significantly inhibits boiler heat transfer rates, thus, reducing energy efficiency. As with boilers in other industrial plants, these risks are alleviated by altering the boiler chemistry with chemical additives. Corrosion is prevented when various chemicals (for example tri-sodium phosphate Na_3PO_4 , ammonia) are used to raise the boiler water pH to a well-defined alkaline range. These additives also prevent calcium-based scale. The relatively high pH value also serves to prevent magnesium-based scale because magnesium hydroxide precipitates as well. In addition to such a treatment programme, polymers and chelants may be added for improved corrosion and scale prevention. Well-known industrial guidelines for the quantities of these additives have been provided [33].

Process condensates from the deaerator stream will also appear in the boiler blow down. Their volume is low compared to the rest of the boiler blowdown and contain similar contaminants. In addition, low levels of ammonia and biodegradable organics result from the reuse of the process condensates as make up water to the deaerator.

Given these constraints, the environmental objective of minimising the steam contamination translates into the task of appropriately monitoring and controlling the boiler chemistry such that these guidelines are followed. Feed water sources of higher quality would also serve to reduce the need for chemical additives. Such opportunities can be investigated upon integration with nearby industrial facilities.

BAT is therefore to manage the process chemistry in line with the available water source and integrate where possible with nearby facilities.

5.3.11 Cooling water blowdown

The cooling water blowdown can be found as an effluent stream when the facility has decided to use a semi-open recirculating system. The emissions are required to balance corrosion, scale, and bio-fouling. These objectives are further complicated by efforts to reduce water consumption. Many of the best available techniques to minimise these emissions can be found in reference 24.

5.4 Waste aspects

The impact of waste from SMR-based hydrogen production units does not warrant process-specific abatement techniques. Instead, the appropriate common industrial practice is described in this section [8, 34].

Description

Due to its process and design, SMRs generally have little potential for waste generation. To meet legal obligations and requirements it is necessary to define the categorisation and type of waste together with the requirements for waste storage, handling, transfer and disposal (European Waste Catalogue Code and Labelling) [35].

Appropriate waste management shall be applied, i.e. selecting the highest practicable option from the following waste hierarchy:

- prevention and minimisation of waste at source;
- maximum recycling and reuse of materials and energy; and
- safe disposal of waste that cannot be reused or recycled in the following order of options:
 - physical, chemical or biological treatment;
 - incineration; and
 - landfill.

To meet legal obligations and requirements it is necessary to:

- describe the waste in sufficient detail to provide enough information to enable any subsequent handlers of the waste to manage it correctly and safely;
- define the categorisation and type of waste (European Waste Catalogue Code and Labelling) [35];
- define waste quantities generated;
- define the requirements for waste storage and handling; and

- define waste treatment, transfer and disposal.

Minimisation of wastes should consider the following aspects:

- applied methods of catalyst performance monitoring;
- design for and adherence to extended lifetimes of each type of catalyst;
- major plant overhaul frequencies;
- volumes of each type of catalyst and solutions;
- used waste catalyst removal methods;
- waste catalyst disposal / recycling methods;

The principle of all waste management is to avoid when possible and to minimise the generation of wastes. Hence, appropriate process design and catalyst performance monitoring methods shall be applied to prolong catalyst lifetime.

5.4.1 Solid waste

Description of waste

SMR generates relatively few solid wastes which can be clustered as follows [8, 30]:

- Catalysts, absorbents and adsorbents:
 - Feed hydrogenation catalyst.
 - Feed purification catalyst.
 - Feed purification absorbent.
 - Reforming and pre-reforming catalyst.
 - Shift catalyst.
 - PSA and TSA (dryer) adsorbents.
 - Post reformer catalysts.
- Technical Materials:
 - Insulation (mineral wool, ceramic fibre, etc).
 - Coldbox perlite (insulation).
 - Refractory (reformer, WHRU).
 - Scrap metals (piping, etc.).
 - Electrical (motors, cable, lighting, etc).
 - Instrumentation (transmitters, modules, etc).
 - Used equipment (for example reformer tubes, end-of-life equipment).
- Sludges:

- Oil interceptor sludge.
- Cooling tower basin.

Typically, these wastes are generated during a plant maintenance period, except for catalysts which have several years of life expectancy, even months for desulfurising materials. Strict industry standard controls are implemented to deactivate used catalysts and to minimise any uncontrolled release to the environment.

Operational data

Typical waste disposal / recycling methods [36]:

- Feed hydrogenation catalyst: recovery as raw material feedstock in production of Mo and Co ferro-alloys. Care shall be taken in handling these catalysts as they can be self-heating when exposed to air, leading to high temperatures and sulphur compounds release exposure to air should be minimised at all times.
- Feed purification catalyst: recovery of valuable base metals should be performed by approved contractors and in compliance with all applicable regulations on waste treatment.
- Feed purification absorbent: recovery as raw material feedstock in production of Zn metal or Zn chemicals. Alternatively, used absorbent (ZnS) is stored on waste disposal units.
- Reforming catalyst: recovery as raw material feedstock in production of Ni, Ferro Nickel or Stainless Steel.
- Shift catalyst: recovery as raw material feedstock in production of ferro alloys, Cu and Zn metal/cathodes. Care shall be taken in handling these catalysts after use as they are pyrophoric.
- Catalyst disposal and recycling is described in EIGA Doc 230, *Safe Catalyst Handling in HyCO Plants* [36].
- Product Purification (PSA) or dryer Temperature Swing Adsorption (TSA) Adsorbent: disposal to landfill.

Spent adsorbents (material) should be disposed of immediately or stored in a manner that will not impact the environment until disposal can be arranged. It is recommended that spent material be stored in discrete containers such as drums or portable containers for each different material type. If containers are not feasible, spent material should be stored on an impermeable surface such as concrete, asphalt or plastic sheeting that is heat and chemical resistant. It is recommended that spent material be protected from rainfall to prevent the possibility of generating contaminated storm water runoff. If water flooding has been used during unloading operations, additional spill prevention and controls such as temporary dykes may be needed to contain free liquid that can be generated when the spent material is unloaded.

- Product purification activated carbon: disposal to landfill.
- Insulation Materials (mineral wool, ceramic fibre): disposal to landfill.
- Coldbox perlite (insulation): thermal recycling or recycling and purification for new product (see EIGA Doc 146, *Perlite Management* [37]).
- Scrap metals (pipework, etc.): recovery as raw material feedstock in production of new metals.
- Electrical (motors, cable, lighting): recovery as raw material feedstock in production of new metals.

- Instrumentation (transmitters, modules, etc.): recovery as raw material in production of new metals when feasible.
- Batteries: separate collection and recovery.

Applicability

All.

Economics

Typical costs / savings associated with catalyst disposal / recycling are country dependent.

Driving force for implementation

To reduce solid waste to landfill – increasing costs and regulation.

Achieved environmental benefits

Waste management reduces waste quantities, and the release of pollutants into the environment.

Cross-media effects

Depending on the waste disposal method applied, cross-media may have to be evaluated.

Reference literature

Catalyst supply and recovery vendor literature provide generic information on appropriate handling and disposal methods.

5.4.2 Liquid spill

In addition to above assessment liquid spills shall be managed by application of additional measures. Plant areas in which liquid spills could occur shall be appropriately designed to collect such spills and to prevent any soil contamination. Such appropriate design means include, for example:

- spill resistant ground sealing (concrete plate, paving or plastic covers) with pits accessible for regular controls (leakage inspections);
- appropriate containments and storage facilities for oil, lubricants or other liquid chemicals as aqueous amine solutions, water treatment chemicals out of the carbon dioxide washing system; and
- avoiding underground storage vessels or tanks (since these are more difficult to control and inspect).

In the event of spillage of liquid waste adequate procedures and emergency plans shall be available. These should regulate how, for example:

- spillage is contained as quickly as possible (using, for example, spill kits);
- to prevent spillage entering the drainage system (and to inform the relevant authorities immediately in such a situation); and
- materials which were used to adsorb spillage are stored and disposed of correctly.

5.5 Use of refractory ceramic fibres

Description

Alumino-silicate fibres, also known as refractory ceramic fibres (RCF), are used for the insulation of high temperature reformer furnaces.

RCFs are one of a number of high temperature insulation wools. RCFs are used in applications where other wools cannot be used due to temperature, environment, etc. RCF is a generic name that covers both alumino-silicate refractory ceramic fibres (Al-RCF) and zirconia alumino-silicate refractory ceramic fibres (Zr-RCF).

In reformer furnaces, refractory ceramic fibres are used in locations where the temperature exceeds 1000 °C under continuous operation or is likely to exceed 1100 °C during limited periods.

RCFs are installed in the radiant section of the furnace, where the temperature can reach 1200 °C locally, and are present at the entrance of the flue gas duct, where the temperature of the flue is close to 1100 °C in normal operation. Further downstream, heat recovery cools down the flue gas.

RCFs are present in articles of various forms and shapes according to the needs, see EIGA Doc 207, *Safe Operation and Maintenance of Furnaces Insulated with Refractory Ceramic Fibres (RCF)*, for more details about precise locations depending upon the type of use [38].

RCFs are classified under Regulation (EC) No 1272/2008 *on classification, labelling and packaging of substances and mixtures* (CLP) as a carcinogen, Carc. 1B1 (H350i: *May cause cancer by inhalation*) [39].

Exposure to any type of fibres (regardless of classification) requires that proper workplace protection measures and good work hygiene practises should be used when working with all high temperature insulation wool (HTIW) products. In general, the exposure to fibre dust should be minimised during site activities by the use of equipment and procedures that minimise dust production. If possible, only products that are preassembled and cut to fit should be used.

The Chemical Agents Directive (CAD) and the Carcinogens or Mutagens Directive (CMD) require employers to conduct workplace specific risk assessments in order to eliminate or minimise risk, preferably by substitution of a non-hazardous or less hazardous process or chemical agent [40, 41].

Workplace safety is controlled by providing and maintaining control measures identified in the employer's risk assessment. Control measures include periodic measurements to verify that established occupational exposure levels ("indicative occupational exposure limit values" or "IOELV", and "binding occupational exposure limit values" or 'BOELV') are not exceeded.

Under REACH regulation, RCFs have been included in the candidate list of substances of very high Concern (SVHC) [42]. REACH requires the progressive replacement of SVHCs from supply and use through authorisation and restriction [42].

The REACH registration dossier identifies risk management measures that need to be implemented to show that the relevant derived no exposure limit (DNEL) or derived minimal effect level (DMEL) will not be exceeded [42].

For information, the European binding Occupational Exposure Limit (BOELV) has been proposed at 0.3 fibres/ml.

Under CMD, substitution is mandatory when technically feasible [40].

Applications can be very different even in the same industrial sector. Therefore, the evaluation of the feasibility to substitute shall be done case by case. TRGS 619, an official recommendation from the German ministry of labour and social affairs, may be used as a guideline to precisely and specifically analyse an application [43]. Finally, a test under representative industrial conditions should confirm the adequacy of the alternative.

Not only temperature but also chemical stability and physical behaviour are important areas to look at before a decision on alternative material or method is taken. For example, Alkaline Earth Silicate (AES) wools do not have similar physical and chemical properties compared to Alumino Silicate Wools ((ASW)

for high temperature applications. In particular, they will not withstand the high temperature reducing atmosphere (more than 800 °C) present in steam methane reforming furnaces.

Furthermore, any change will involve considerable cost and should only be considered where alternatives are well proven, technically safe and economically feasible.

Achieved environmental benefits

Increased lifetime of refractory and reduced waste.

Cross-media effects

None.

Operational Data

As above.

5.6 Environmental management systems

Description

The essential elements of an environmental management system are described in many sources, and applicable in principle for all sectors [44]. For the BREF guidance documents these is standard text for example found in Section 4.15.1 of the BREF on Refining of Mineral Oil and Gas [3].

A summary for the industrial gases industry is found in EIGA Doc 107, which provides a guide to implementation of an environmental management system according to EN ISO 14001 [30, 34].

EIGA Doc 122 identifies specific important environmental aspects and impacts to be identified and managed in operation and guidelines for so doing including [8]:

- energy;
- noise;
- emissions to air and water;
- the consumption of natural gas feed and water consumption;
- use and management of waste catalyst material; and
- use of consumables such as lubricants, nitrogen, compressed air, other utilities, adsorbent materials.

Achieved environmental benefits

The overall effective management of the installation minimises environmental and other impacts.

Reference literature

Additional guidance is provided in EIGA Doc 88, *Good Environmental Management Practices for the Industrial Gas Industry* [45],

Standard Reference literature also includes:

- Regulation (EC) No 1221/2009 *on the voluntary participation by organisations in a Community eco-management and audit scheme (EMAS)* [46];

- DG Environment EMAS website [47]; and
- EN ISO 14001, and ISO 14000 family of standards [34].

5.7 Plant improvement and plant revamps

Description

As plant and equipment ages and especially after around 20 years of plant life, improvements and revamps to improve efficiency should be considered. In addition, process improvement techniques such as plant debottlenecking may be used to optimise the plant conditions to the current supply arrangements, which can be different from those when the plant was first built (for example new or different customers, different product supply balance etc). Typical items that can be considered for plant revamps are:

- replacement of burners with improved / lower NO_x types (see 5.3.1.3 and 5.3.1.4);
- additional capacity such as adding pre reformer or other plant debottlenecking;
- extended preheating of feed;
- new or full overhaul of heat exchangers, radiant coils;
- new or full overhaul of compressors; and
- boiler or cooling water system improvements.

Achieved environmental benefits

- Energy efficiency improvements, capacity increases.
- NO_x reduction, waste reduction.
- Reduction in maintenance and associated wastes.

Cross-media effects

Shut down and major equipment overhaul can generate additional wastes.

Operational Data

None.

Applicability

All.

Economics

Typical costs / savings associated with energy efficiency improvements have to be evaluated against the capital cost and are not usually economic for plants less than 20 years old.

Driving force for implementation

To reduce NO_x emissions, reduce waste; improve capacity and energy efficiency, if necessary, to match current capacity with current demand.

6 References

Unless otherwise specified, the latest edition shall apply.

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Appendix A – Process variability for hydrogen production plants

Option		1	2	3	4
Description		Standard	Min Energy	Max Export Steam	High Efficiency (min CO2)
Investment Level		basis	++	+	+
Characteristic Process Features	Shift Type	HT	MT	HT	HT
	Pre-Reformer	NO	YES	NO	YES
	Air Preheat	MEDIUM	MEDIUM	NO	HIGH
Performance Figures	Unit				
NG-Feed	Nm ³ /h	19 575	19 077	18 576	18 316
NG-Fuel	Nm ³ /h	2 245	2 833	5 499	1 096
NG-Total	Nm ³ /h	21 820	21 910	24 075	19 413
Steam Export (Battery Limit)	kg/h	40 790	50 843	63 478	8 731
H2 Product	Nm³/h	50 000	50 000	50 000	50 000
Specific Feed+Fuel Consumption	Nm ³ /Nm ³	0,436 <i>100,0%</i>	0,438 <i>100,4%</i>	0,481 <i>110,3%</i>	0,388 <i>89,0%</i>
Specific Energy Consumption (*)	GJ/1000Nm ³	13,07 <i>100,0%</i>	12,49 <i>95,6%</i>	13,24 <i>101,3%</i>	13,41 <i>102,6%</i>
Flue Gas Flow Rate	Nm ³ /h	121 782	123 239	147 493	94 018
CO2 in Flue Gas	kg/h	43 145 <i>100,0%</i>	43 382 <i>100,6%</i>	47 617 <i>110,4%</i>	38361 <i>88,9%</i>
Process parameters					
Air Preheat Temperature	°C	265	274	20	680
Indicative NOx (typical)	mg/m3				

(*) Specific Energy Consumption = (LHV (Feed+Fuel) - Enthalpy Export Steam) / 1000 Nm³/h H2

LHV = low heating value

SI Notation: decimal separator is "comma" (3/2 = 1,5) and thousand is separated by "dot" (1000 = 1.000)