



**BEST AVAILABLE TECHNIQUES
FOR THE CO-PRODUCTION OF
HYDROGEN, CARBON MONOXIDE
& THEIR MIXTURES BY STEAM
REFORMING**

IGC Doc 183/13/E

EUROPEAN INDUSTRIAL GASES ASSOCIATION AISBL



AVENUE DES ARTS 3-5 • B-1210 BRUSSELS
Tel: +32 2 217 70 98 • Fax: +32 2 219 85 14
E-mail: info@eiga.eu • Internet: www.eiga.eu



BEST AVAILABLE TECHNIQUES FOR THE CO-PRODUCTION OF HYDROGEN, CARBON MONOXIDE & THEIR MIXTURES BY STEAM REFORMING

PREPARED BY :

STEPHEN BRADLEY	AIR PRODUCTS
JEAN DUCROCQ	AIR LIQUIDE
JEAN GALLARDA	AIR LIQUIDE
BERNARD MINEUR	AIR LIQUIDE
WOLFGANG OTT	LINDE GROUP
ANDRE RITTER	LINDE GROUP
PHILIP BRICKELL	EIGA

Disclaimer

All technical publications of EIGA or under EIGA's name, including Codes of practice, Safety procedures and any other technical information contained in such publications were obtained from sources believed to be reliable and are based on technical information and experience currently available from members of EIGA and others at the date of their issuance.

While EIGA recommends reference to or use of its publications by its members, such reference to or use of EIGA's publications by its members or third parties are purely voluntary and not binding.

Therefore, EIGA or its members make no guarantee of the results and assume no liability or responsibility in connection with the reference to or use of information or suggestions contained in EIGA's publications.

EIGA has no control whatsoever as regards, performance or non performance, misinterpretation, proper or improper use of any information or suggestions contained in EIGA's publications by any person or entity (including EIGA members) and EIGA expressly disclaims any liability in connection thereto.

EIGA's publications are subject to periodic review and users are cautioned to obtain the latest edition.



Table of Contents

1. Introduction	1
2. Scope and purpose	1
3. Definitions and publication terminology	1
3.1. HyCO	1
3.2. Syngas	1
3.3. Publication terminology	1
3.3.1. Shall	1
3.3.2. Should	1
3.3.3. May	1
3.3.4. Can	1
4. Co-production of hydrogen, carbon monoxide and syngas by steam reformers and coldbox	2
4.1. Steam Reforming Process	2
4.1.1. Steam reforming process equipment	3
4.1.2. Indicative process flows for HyCO production	4
4.2. Steam Reforming Process: Environmental Advantages & Impacts	6
5. Existing Best Available Techniques	7
5.1. Energy Efficiency Management System Techniques	7
5.2. Membranes	8
5.3. Plant initial start-up	9
6. Additional BATs to address Emissions to Air	10
6.1. Low Excess Air	10
6.2. Low NOx Burners Description	10
6.3. Pre-reforming	11
6.4. SCR – Selective catalytic reduction	12
6.5. SNCR – Selective Non Catalytic Reduction	13
6.6. Oxygen and/or carbon monoxide monitoring	14
6.7. Carbon monoxide leak prevention	14
6.8. Utilisation of sulphur free tail gas	15
6.9. Integrated monitoring scheme rationalization	16
6.10. Cryogenic gas disposal system	17
7. Noise abatement methodology	17
8. Energy efficiency	18
8.1. Optimum steam/carbon ratio and associated measurement	18
8.2. Air preheat	19
9. Emissions to water	20
9.1. General waste water management strategy	20
9.2. Process condensates	21
9.3. Boiler blow down	21
9.4. Cooling water blow down	21
10. Other waste aspects	22
10.1. Solid wastes	23
10.2. Use of RCF (Refractory Ceramic Fibres)	25
11. Environmental Management Systems	26
12. Process improvements and plant revamps	26
13. References	27

1. Introduction

This EIGA publication provides guidance to EIGA members specifically to site managers, technical managers, and company environmental specialists on some best available techniques for the co-production of hydrogen, carbon monoxide and their mixtures by steam methane reforming.

2. Scope and purpose

This document provides guidance on compliance with EC Directive 2008/1/EC Integrated Pollution Prevention & Control [2], further recast into EC Directive 2010/75/EU Industrial Emissions [2bis] and associated BREFs.

The main objectives are

- To propose techniques deemed as best and available for steam methane reformer plants with one or multiple products.
- To gather data to support conclusions on Best Available Techniques.
- To encourage consistency with associated BREFs about hydrogen, carbon monoxide, and syngas production.
- To contribute to the European IPPC Bureau's reference documents[12] that are due for revision and that are associated with hydrogen, carbon monoxide and syngas production technologies.

This document specifically addresses the co-production of hydrogen, carbon monoxide, and their mixtures by steam reforming. In that regard, this document is a sister to EIGA Doc.155 [37] which focuses primarily on the best available techniques of steam reforming where hydrogen, (beside the co-produced steam) is the only product.

3. Definitions and publication terminology

3.1. HyCO

HyCO in the document refers to the entire process in Figures 2, 3, 4, 5, 6. The front end process is often called steam methane reforming, especially when methane is used as the feedstock. Meanwhile, the steam (methane) reformer refers only to the fired chemical reactor in which Reaction 1-3 take place.

3.2. Syngas

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

3.3. Publication terminology

3.3.1. Shall

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

3.3.2. Should

Indicates that a procedure is recommended.

3.3.3. May

Indicates that the procedure is optional.

3.3.4. Can

Indicates a possibility or ability.

4. Co-production of hydrogen, carbon monoxide and syngas by steam reformers and coldbox

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 [37]. These process technologies include:

- Steam reforming of light feedstock (e.g. methane or naphtha)
- Auto-thermal reforming.
- 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 the available feedstock. This hydrogen/carbon monoxide split (H_2/CO split) 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 document, 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.

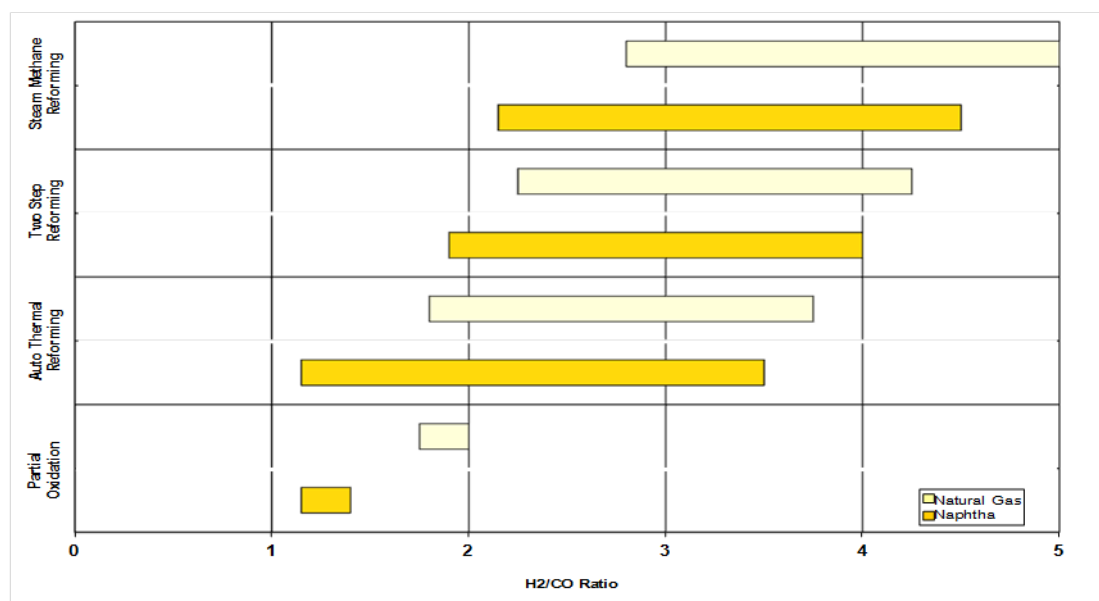


Figure 1. H_2/CO split for HyCO Process Technologies [37, 8]

This document seeks to focus solely on the steam reforming process because of the wide coverage of H_2/CO split. Specifically, it 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.

4.1. Steam 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 typically are:

- desulphurization unit,
- steam methane reformer (SMR); note that pre-reforming is addressed in section 6.3.
- carbon monoxide shift unit

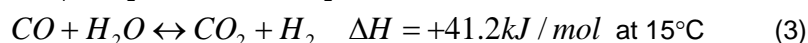
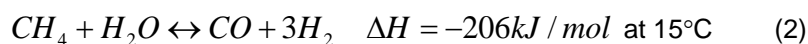
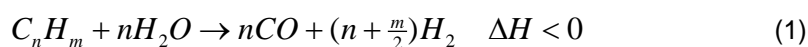
- carbon dioxide removal by chemical wash
- dryers & cold box
- pressure swing adsorption (PSA)
- membranes

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.

4.1.1. Steam reforming process equipment

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

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



These equations apply for either methane or heavier feedstock respectively[5]. These reactions are achieved by passing the steam/feedstock mixture through the reformer tubes filled with a (usually nickel-based) catalyst. Because the first two reactions dominate, the reaction overall is highly endothermic and reformer gas outlet temperatures are in the range of 750-1000°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 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 products split (see fig 3 below 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 (e.g. iron-chromium, copper alloys) [4]. 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 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 (e.g. MDEA, MEA, aMDEA) may be used to complete the chemical wash. However, aMDEA is most commonly used in modern plants for its greater energy efficiency.

Adsorbers (dryers) & 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 in 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.

Pressure swing adsorption: the PSA serves to purify hydrogen. The remaining PSA tail gas that contains primarily carbon monoxide, hydrogen, methane, carbon dioxide and water is usually fed to the reformer as the main fuel. [4]

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.

4.1.2. Indicative process flows 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 flows to demonstrate the flexibility of the process.

Figure 2 demonstrates a typical process flow for the co-production of hydrogen, carbon monoxide and steam. 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. Steam is produced by heat recovery with the hot process gas plus hot flue gas. Depending on required H₂/CO split, carbon dioxide may be recycled.

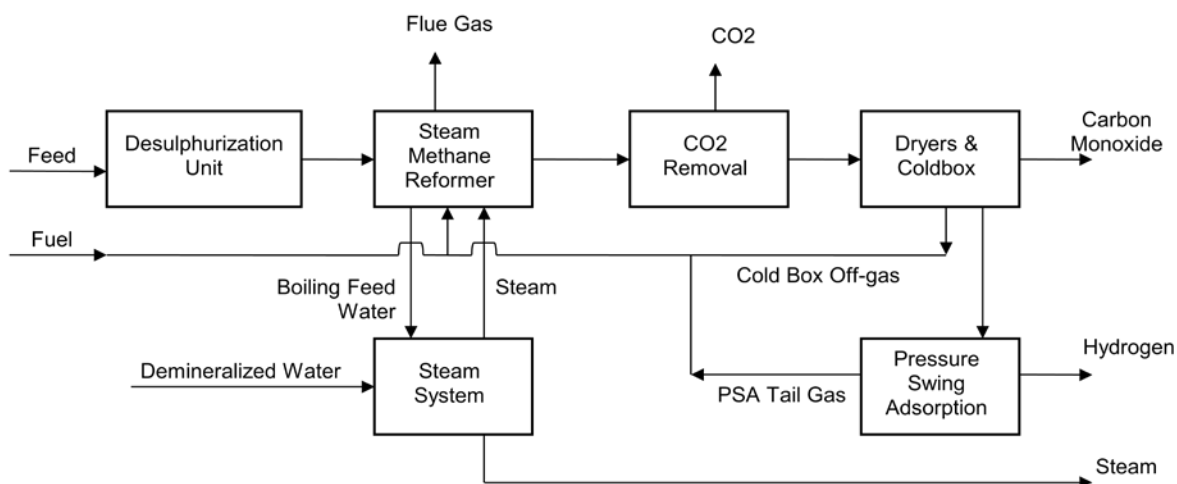


Figure 2. Co-production of hydrogen, carbon monoxide and steam

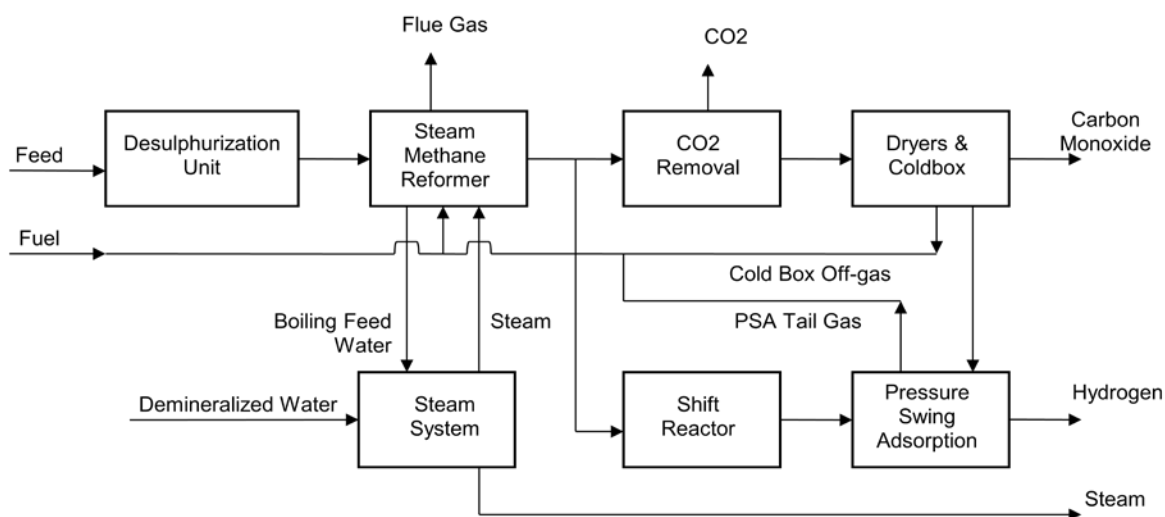


Figure 3. Co-production of hydrogen, carbon monoxide and steam along with a shift reactor

Figure 3 adds a shift reactor in parallel to carbon dioxide removal. This serves to increase the H₂/carbon monoxide split over a similar design that might follow the process flow shown in Figure 2. Of course, if there is no carbon monoxide production at all, the carbon dioxide removal unit and cold box may be removed to yield a hydrogen only solution as is described in EIGA Doc 155. [37]

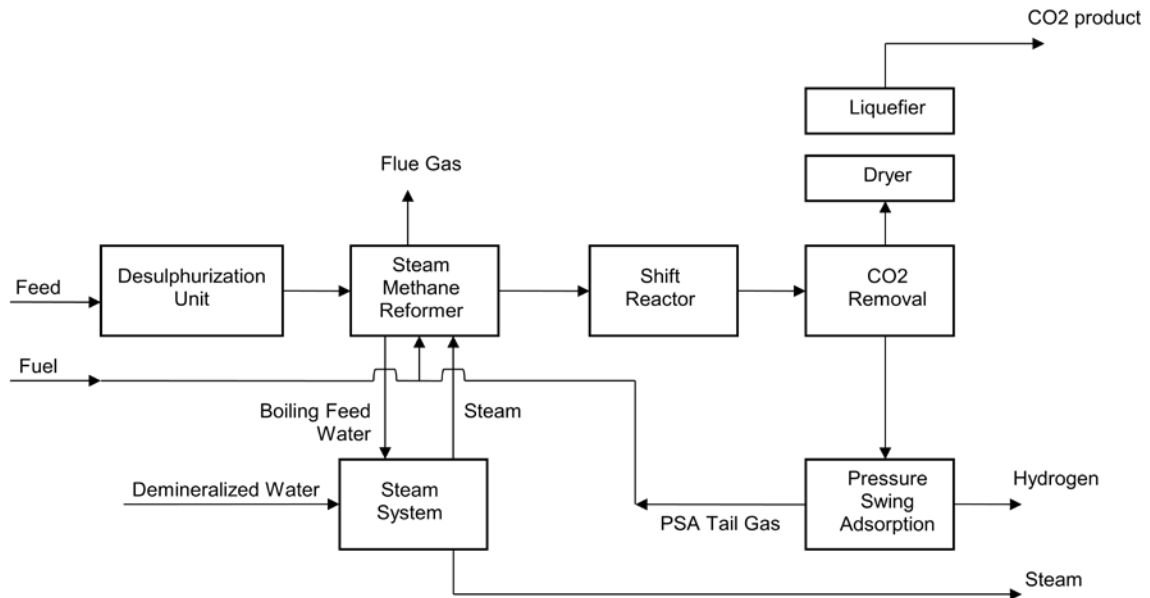


Figure 4. Co-production of hydrogen and steam with complementary carbon dioxide production

Figure 4 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.

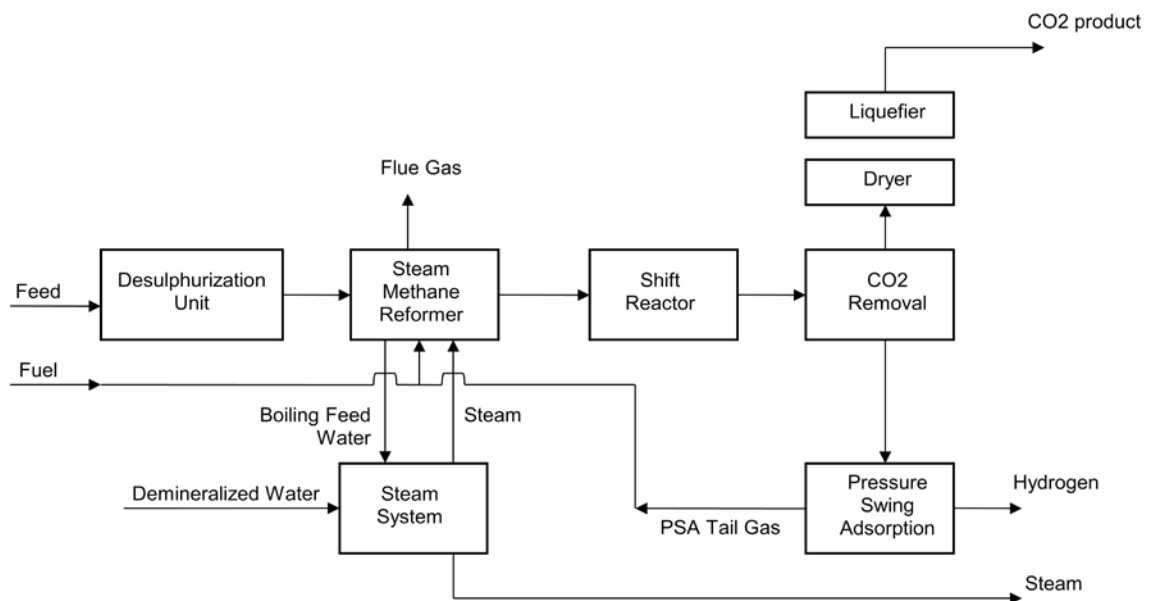


Figure 5. Production of carbon monoxide and steam

Figure 5 demonstrates the case where carbon monoxide is the only product. 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 of the cold box has a large quantity of hydrogen (amongst other constituent gases), and its heating power is used in the fuel stream. Note that hydrogen recycle to desulphurization unit as represented here applies also to any other scheme.

Figure 6 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 PSA.

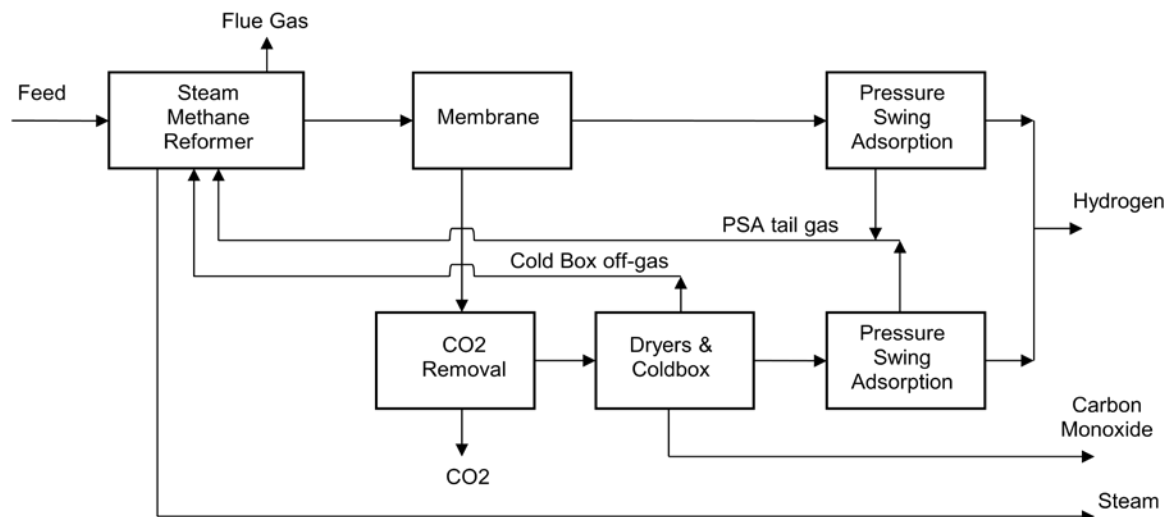


Figure 6. Use of membranes for H₂ and carbon monoxide production

4.2. Steam Reforming Process: Environmental Advantages & 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 [6]. First, the process generates few wastes, chemical storage, or liquid effluents. None of these are particularly hazardous [7]. Sections 9 and 10 describe good practice to limit these environmental aspects while Section 11 introduces elements of an appropriate environmental management system.

Steam reforming is also advantageous from a product yield and energy consumption point of view. As seen previously, Figure 1 shows the product yield ranges for four industrial processes in terms of the ratio of hydrogen to carbon monoxide. Normally steam reforming results in a H₂/CO ratio of about five. By recycling the carbon dioxide, separated in the chemical wash unit, H₂/CO ratio can be reduced to a value of approx. three. If a lower H₂/CO ratio is required, additional carbon dioxide can be imported. Hence HyCO plants including steam reforming enables a very flexible plant operation.

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 HyCO steam reforming process can be recycled into the process.

Furthermore 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. In light of this, steam reforming may be considered to have the smallest carbon-footprint of all hydrogen production processes¹[4].

The remaining air emissions can be addressed individually. The use of light hydrocarbon feedstock, and natural gas in particular, reduces the potential for carbon monoxide, particulates and SO_x emissions. SO_x emissions are particularly reduced due to the necessary presence of the desulphurizer [7]. Finally, the process' need for highly elevated temperatures increases the potential for NO_x emissions [10]. This aspect is particularly affected by energy efficiency measures that often raise reformer temperatures further. However, this aspect is partially abated with the recirculation of carbon dioxide-rich PSA tail gases which reduce flame temperatures in the reformer. Additional measures are described in the following section.

¹ Assuming that both direct and indirect emissions are counted, and that the energy mix of electricity production of the EU is used.

5. Existing Best Available Techniques

5.1. 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.

In addition several techniques can be used to integrate the energy usage of the carbon monoxide separation system and to improve overall plant efficiency by energy optimisation of carbon dioxide wash unit, adsorber station /dryers and carbon monoxide coldbox. For example :

- Use of syngas or low pressure steam to regenerate carbon dioxide-loaded MDEA in the carbon dioxide removal system,
- Optimize heat integration by usage of cold streams from the cold box for pre-cooling of warm streams,
- Recycle of coldbox off-gas,
 - Better feedstock usage by carbon dioxide recycle.

An efficiency evaluation at the plant design stage should be used to identify these issues and input into the design process, referring to the range of energy efficiency techniques as described in Refinery BREF (Section 4.10.1.3 Heat integration/recovery and Section 4.10.1.4 Steam management) [1]. 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 Energy Efficiency BREF [12].

Achieved environmental benefits

These measures increase energy efficiency of the HyCO plant and any associated facility, thus reducing green house 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 3.000 – 3.600 Nm³ of hydrogen per ton of feedstock.

Achieving values as low as 20.000 MJ/t hydrogen requires not only to use BAT such as efficient heat recovery contained in fumes by preheating feed process, 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 can achieve up to 80 - 90 % of the required energy for steam reforming depending upon the way reforming is conducted.

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 to 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.

One can compare such Table 1 values to those published elsewhere such as Sema and Sofres, 1991 where values ranging from 35.000 up to 80.000 MJ/t hydrogen are mentioned. 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.

Fuel (MJ/t H ₂)	Electricity (kWh/t)	Steam produced (kg/t)	Cooling water (m ³ /t, $T=10^{\circ}\text{C}$)
20.000 – 30.000	200 - 400	2.000 – 8.000	25 - 100

Table 1 : requirements for steam reforming based on recent large size equipment including BAT on energy efficiency

Economics

Operational costs.

Driving force for implementation

Increasing energy efficiency and thus reducing green house gas emissions.

Example plants

There are many examples of energy optimisation driven strongly by economic as well as environmental benefits.

Reference literature

Energy efficiency BREF [12].

5.2. 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. Pre-heater, filter 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, ie water cooling, but the impact is not significant.

Operational data

No information provided.

Economics

Low additional investment and operating costs.

5.3. 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 (e.g. minimum load operation, action of safety devices as per design, etc.),
- Verify compliance with environmental operating permit requirements such as emissions limits.

Preparation for the performance tests requires a start-up, adjustment of sub-processes and controller tuning as well as demonstration of a stable operation, check of equipment and control functionality. This frequently requires shut downs 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 is necessary. Consequently the performance test is structured and optimized to ensure minimum wastage of product and to minimize emissions from venting and flaring.

Achieved environmental benefits

Verification of unit's performance including environmental operating permit requirements and at the same time minimizing 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 optimized to minimize 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 [39].

6. Additional BATs to address Emissions to Air

Due to the low sulphur gas firing only NO_x and carbon monoxide have to be considered as relevant emission components.

6.1. Low Excess Air

One existing best available technique for the abatement of NO_x emissions is to use a relatively small quantity of excess air. Steam methane reforming typically requires 10% excess air with the minimum value being limited by safety considerations. Further details on this technique can be found in the Large Combustion Plant BREF[11].

6.2. Low NO_x Burners Description

Low-NO_x burners are used to burn PSA tail gas and other gaseous fuels. This technology in steam reformers (SMR) for hydrogen production is considered to be a BAT. Air staging, fuel staging and flue gas recirculation as described in the Large Combustion Plants BREF [11] are not as such applicable for the furnace design of SMRs but are applied in the low-NO_x burner design. For further information on low-NO_x burner types see Chapter 4.10.4.1 of Refineries BREF[1]. Further SMR specific aspects to be considered for burner type selection are described in the section on operational data below.

Achieved environmental benefits

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.

Cross-media effects

No negatives. The application of gaseous fuel also minimise SO₂ emissions.

Operational Data

In order to provide stable operation of the SMR, low NO_x burners design has to be selected carefully with regard to operating conditions required for the specific cases. Applicable low-NO_x burner type and achievable emission levels depend on the specific situation. The following constraints have to be considered:

- SMR reaction requires high reforming temperatures (around 750-1000 °C)
- specific fire box geometry (long heated tubes, rectangular box etc.)
- turndown rate
- feed composition flexibility
- extend of air preheating
- even air/fuel mixing to prevent carbon monoxide and unburned hydrocarbon emissions
- composition range of available supplementary fuel gas

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

Typical NO_x emission values (calculated as NO₂ in dry flue gas with 3 vol-% O₂) when the fuel does not include significant nitrogen content:

- i) without air preheat: 200 to 240 mg/Nm³ (100-120ppmv).
- ii) with air preheating: up to 300 mg/Nm³ (150ppmv).

Increased NO_x emission values compared to pure hydrogen plants (see EIGA Doc.155 [37]) are due to higher firing temperatures as needed for the process and use of different fuel gas compositions : less inert gas and higher hydrogen content in the PSA purge gas fed back to burners.

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

Applicability

Low-NO_x burners are most suitable for gas-fired-based SMRs. Application is straightforward for new installations. Applicability of retrofitting of low-NO_x 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 Refineries BREF[1].

Economics

For achievement of lower figures, techniques such as SCR (see 6.4) and SNCR (see 6.5.) should be considered.

The investment cost of low NO_x burners is typically in the range of 105 to 150% of that of conventional gas fuel burners.

Driving Force for Implementation

Reduction of NO_x emissions.

Example Plants

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

Reference Literature

Large Combustion Plant BREF[11].

6.3. 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 have to 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);
- higher catalyst waste generation rate since pre-reformer catalysts is highly reactive and needs to be exchanged more often (typically once per year).

Operational Data

No information provided.

Applicability

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

Economics

Additional investment and operating costs.

Driving Force for Implementation

Conversion of steam savings to fuel gas savings.

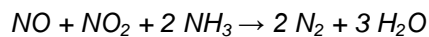
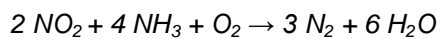
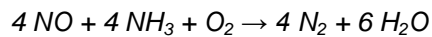
Reference Literature

Mineral Oil and gas Refineries BREF [38].

6.4. SCR – Selective catalytic reduction

Description

Selective catalytic reduction (SCR) is a means of converting nitrogen oxides (NO_x) with the aid of a catalyst into diatomic nitrogen (N₂) and water (H₂O). In SCR systems, ammonia vapour is used as the reducing agent and is injected into the flue gas stream, passing over a catalyst. NO_x emission reductions over 70-95% [1] are achieved. The optimum temperature 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 NO_x concentrations in the flue gas at the economiser outlet. The temperature of the flue gas in the SCR reactor is controlled by mixing the flue gas exiting the economiser with the flue gas from the economiser bypass. 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 are used in an air preheater.

Achieved environmental benefits

Commercial selective catalytic reduction systems have been shown to reduce NO_x by 70-95%. [1]

Cross-media effects

Compared to steam reforming process without SCR the following cross-media effects have to be taken into account:

- additional reducing agent such as ammonia required: ammonia slip leads to ammonia emissions;
- higher catalyst waste generation rate (typically once every 3 years).

Operational data

No information provided.

Applicability

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

Economics

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

- higher investment costs (additional SCR equipment);
- higher operating costs (additional reducing agent such as ammonia required and additional power is required due to increased pressure drop and potentially required auxiliary blower for dosing).

Driving force for implementation

Reduction in NO_x emissions.

Example plants

There are some examples of SMRs using SCR.

Reference literature

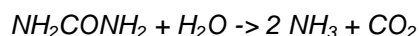
Steam: its generation and use, The Babcock & Wilcox Company [40].

6.5. SNCR – Selective Non Catalytic Reduction

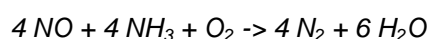
Description

The process involves injecting either ammonia or urea into the flue gas at a location where the flue gas is between 760 and 1,093 degree Celsius (1,400 and 2,000 °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:



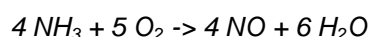
The reduction happens according to (simplified)



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 reduced. 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, time, and mixing often lead 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 isn't there.

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.

Economics

Compared to steam reforming process without SNCR additional investment and operating costs have to be taken into account:

- higher investment costs (additional SNCR equipment),
- 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

Duo et al., 1992 [41].

Steam: its generation and use. The Babcock & Wilcox Company [40].

6.6. 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 is typically controlled to get 2% excess oxygen in the flue gas corresponding to approximately 10% excess air flow. So 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 adapts 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% excess oxygen in the flue gas.

Applicability

All HyCO plants

Economics

Fuel consumption is optimized.

Driving force for implementation

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

6.7. Carbon monoxide leak prevention

Description

Carbon monoxide is flammable in air over a very wide range (12.5% – 74%), 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 minimized and only used to connect equipment that may have to be removed for maintenance, e.g. 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 is eliminated as far as 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, e.g. 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 e.g. 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.

All vents from process lines containing carbon monoxide or syngas mixtures under normal operating conditions should always be directed to a flare equipped with pilot burners.

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.

6.8. Utilisation of sulphur free tail gas

Description

The steam methane reforming process requires the desulphurization of the feed so as to prevent catalyst poisoning; this also protects from unexpected spikes in sulphur in the fuel or air. As a result, the tail gas from the PSA and from the cold box, if present for carbon monoxide separation, is free of sulphur. As this recovered gas forms more than 90% of the fuel, SO_x emissions are correspondingly reduced. This also depends on the sulphur content of the supplementary fuel.

Achieved environmental benefits

HYCO plants have minimal SO_x emissions.

Cross media effects

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

6.9. Integrated monitoring scheme rationalizationDescription

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 have to be considered as relevant emission components. Occasional measurements for compliance verification is recommended for SMR's not subject to Directive 2001/80/EC [13] on the limitation of emissions of certain pollutants into the air from large combustion plants

EN 15259 [14] regulates detailed design aspects for the installation of sample ports and measurement planning. 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, e.g. 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 and its heating value.

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 need not 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.

The SMR process is very stable. Therefore, following the methodology provided in the monitoring BREF, occasional measurements (e.g. once every 3 to 5 years) can be regarded sufficient.

Economics

Investment costs for sample ports:

- approx. 1000€ per required sample nozzle;
- approx. 20000€ for platform with access ladder (very much depending on detailed size and equipment arrangement).

The cost of analysis 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, e.g. periodic environmental reporting.

Example plants

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

Reference literature

Monitoring BREF[15]

EN 15259[14].

6.10. Cryogenic gas disposal system

Description

It is necessary to connect the cryogenic hydrocarbon system to a vaporization 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 vaporization 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 vaporization of the cryogenic liquid.

Achieved environmental benefits

Avoidance of release to the atmosphere of large amounts of vaporizing carbon monoxide (toxic) or methane (a major GHG gas).

Cross-media effects

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

Applicability

To all process 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 vaporization rate is a key safety issue for sufficient vaporization and combustion.

7. Noise abatement methodology

Description

A noise evaluation for the plant should be considered at the design stage. A methodology such as IPPC Noise guidance note H3 parts 1 [16] and 2 [17] Sept 2002- Environment Agency or Attachment of the German TA-Lärm issued August 26th 1998[18] could be used to evaluate the potential for noise impact on local receptors on and off site.

The Refineries BREF [1] 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. Where necessary and practical the noise impacts of the HyCOs 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 shut down 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. Reference should be made to EIGA document Doc.85 Noise Management [19] for a suitable list of techniques.

Achieved environmental benefits

Minimisation of the nuisance potential.

8. Energy efficiency**8.1. Optimum steam/carbon ratio and associated measurement**Description

One essential design technique for improving the global thermal balance is the optimization 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 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 un-reacted methane; thus reducing the hydrogen and carbon monoxide output and increasing the risk of carbon deposition[20]. In order to compensate, the reformer outlet temperature is raised [21]. 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 [21], the relative and absolute values depend strongly on the parameters above.

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 (e.g. methanol, acetic acid) will increase.

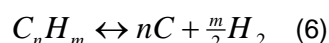
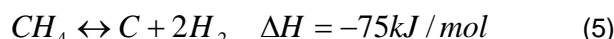
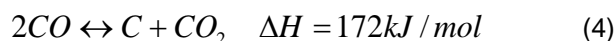
Operational data

The limitation on the S/C ratio is driven by the steam reformer catalyst and depends on feed type, selected parameters, reformer configuration, 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 (see EIGA document 155 section 8.1).

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 [5]:



Such carbon deposition leads to breakdown of the catalyst, further carbon deposits, blockage of the tubes and the development of "hot spots" [5]. 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 [5]. The maximum reformer outlet temperature is limited by mechanical constraints of the reformer tube 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 H₂ 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 (e.g. steam) amongst other variables [21].

Driving force for implementation

The minimal 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 optimized 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.

8.2. Air preheat

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 Refinery BREF[1] needs to be evaluated carefully with regard to the resulting increased NO_x production.

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 green house gas emissions (overall balance).

Cross-media effects

Increased combustion air temperatures increase NO_x emissions from the combustion. Optimised steam production and export to refinery consumers have to be evaluated carefully as adequate alternative without increased NO_x emissions. Reference is also made to the large combustion plant BREF Chapter 7.4.2 [11] and the energy efficiency BREF Chapter 3.1.1 [12].

Operational data

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

Positive effect of air preheating on carbon dioxide emissions has to be balanced against the negative effect on NO_x emissions. Reference is made to Chapter 3.1.1.1 of the energy efficiency BREF [12].

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 energy efficiency BREF Chapter 3.1.1.1 [12]. 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 have to be evaluated carefully.

Driving force for implementation

Increasing energy efficiency and thus reducing green house gas emissions.

Example plants

There are many examples of installed SMRs including air preheating.

Reference literature

Energy efficiency BREF [12]

Large combustion plant BREF[11].

9. Emissions to water

While steam methane reforming does generate a number of liquid effluent streams, they are not sufficiently unique from many other industrial processes to warrant process-specific abatement techniques [6, 7]. Instead, a waste water management strategy can be used to prevent and control the impurities in the different waste water streams. This section describes such a strategy before highlighting specific issues related to the blow downs from the boiler and the cooling tower.

9.1. General waste water management strategy

As stated previously, facilities that co-produce hydrogen and carbon monoxide by steam methane reforming do not generate any particularly unconventional waste water streams. Additionally, these facilities generally exist to serve other industrial facilities (e.g. refineries, acetic acids, cyanates) with liquid effluents that are more challenging to treat. Therefore, a centralized waste water 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 available solution is to divert the liquid effluents from the hydrogen/carbon monoxide co-production facility to the CWWT plant for final treatment.

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 waste water 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.
2. **Stream Segregation & 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.
3. **Minimization of Stream Flow & Contamination** – Once each stream has been identified, segregated, and routed to the appropriate destination, attention can 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 waste water 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.

For further information, EIGA document Doc.122 [6] and the BREF on Common Waste Water and Gas BREF [24] provides some relevant best available techniques in its sections on general environmental management, waste water management, process-integrated measures, and waste water collection.

Given this strategy, for an SMR-based hydrogen/carbon monoxide co-production unit, the following types of liquid effluent streams may have to be considered [6]:

- Demineralised water production unit effluents (if within system boundary).
- Boiler blow down & other process condensates.
- Cooling water blow down.
- Process condensates from synthesis gas cooling.
- Rain/surface water.

- Domestic water.
- Oily water from base plates of pumps and machinery.

Additional liquid effluents may have to be considered for other process plant constellations, e.g. application of liquid feed or co-generation of carbon monoxide.

9.2. 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 waste water

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 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 have to be removed, usually by use of process gas adsorbers. Loaded adsorbers have to be regenerated, e.g. 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 has to be separated. The produced condensate can contain dissolved synthesis gas traces and solvent traces out of the chemical wash (typically amines).

Alternatively, these may be recycled back to the coldbox flash-gas and eventually to the reformer.

9.3. Boiler blow down

Boiler blow down 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 [25]. 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 (e.g. 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 relative high pH value also serves to prevent magnesium-based scale because magnesium hydroxide precipitates as well. In addition to such a treatment program, 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 [25-28].

Process condensates from the deaerator stream will also appear in the boiler blow down. Their volume is low and contain similar contaminants to the rest of boiler blow down. 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 minimizing 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.

9.4. Cooling water blow down

The cooling water blow down 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 minimize these emissions can be found in Sections 4.4 and 4.6 of the Industrial Cooling Systems BREF [27, 29].

10. Other waste aspects

The impact of waste from SMR-based hydrogen production units does not warrant process-specific abatement techniques [27, 30]. Instead, the appropriate common industrial practice is described here.

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 categorization and type of waste together with the requirements for waste storage, handling, transfer and disposal (European Waste Catalog Code and Labeling [31]).

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

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

Achieved environmental benefits

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

Cross-media effects

None.

Operational data

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 categorization and type of waste (European Waste Catalog Code and Labeling [31]);
- define waste quantities generated;
- define the requirements for waste storage and handling;
- define waste treatment, transfer and disposal.

In addition to above assessment liquid spills have to be managed by application of additional measures. Plant areas in which liquid spills could occur have to be appropriately designed to collect such spills and to prevent any soil contamination. Such appropriate design means 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 out of the carbon dioxide-washing system;
- avoiding underground storage vessels or tanks (since these can not be properly controlled or inspected).

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

- spillage has to be 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);
- materials which were used to adsorb spillage are stored and disposed of correctly.

Minimization 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;
- design for minimization of liquid blow down out of carbon dioxide-washing system.

Applicability

All.

Economics

In general, an adequate waste management system leads to overall cost savings and improved economics.

10.1. Solid wastes

This section should reflect solid wastes from carbon monoxide co-production. (e.g. dryer/TSA adsorbents, perlite in coldbox).

Description

The SMR generates relatively few solid wastes which can be clustered as follows [6, 32]:

- Catalysts, absorbents and adsorbents:
 - Feed hydrogenation catalyst.
 - Feed purification catalyst.
 - Feed purification absorbent.
 - Reforming & pre-reforming catalyst.
 - Shift catalyst.
 - PSA and TSA (dryer) Adsorbents.
 - Post reformer catalysts.
- Technical Materials:
 - Insulation (Rockwool, ceramic fibre, etc).
 - Coldbox perlite (insulation).
 - Refractory (reformer, WHRU).
 - Scrap metals (piping, etc.).
 - Electrical (motors, cable, lighting, etc).
 - Instrumentation (transmitters, modules, etc).
 - Used equipment (e.g. reformer tubes, end-of-life equipment).
- Sludges:
 - Oil interceptor sludge.
 - Cooling tower basin.

Typically these wastes are generated during a plant maintenance period and strict industry standard controls are implemented to deactivate used catalysts and to minimise any uncontrolled release to the environment.

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.

Operational data

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

Typical waste disposal/recycling methods:

- 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 pyrophoric.
- Feed purification catalyst: recovery as raw material feedstock in production of road aggregate or cement
- 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.
- Product Purification ("PSA") or dryer ("TSA") Adsorbent: disposal to landfill
- Product Purification Activated Carbon: disposal to landfill
- Catalysts and others: spent catalysts/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 dikes may be needed to contain free liquid that can be generated when the spent material is unloaded.
- Insulation Materials (Rockwool, ceramic fibre): disposal to landfill.
- Coldbox perlite (insulation): thermal recycling or recycling and purification for new product.
- 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.

Reference literature

Catalyst Supply & Recovery vendor literature provide generic information on appropriate handling and disposal methods.

10.2. Use of RCF (Refractory Ceramic Fibres)

Description

“The European Chemicals Agency (ECHA) has recommended to the Commission to include RCF in the list of substances that need authorisation for further placing on the market and use. The authorisation will be limited in time and subject to the demonstration that no suitable and safer alternative substance is available.”

- Following extensive research and testing, there is no technically and economically viable substitute material that has been identified as of today for alumino silicate RCF (according to EN 1094-1 better described as “alumino silicate wool”; ASW) in plants such as steam methane reforming where the refractory lining is exposed to high temperatures (900°C - 1200°C), in a reducing atmosphere for a long duration (several months or years).
- Exposure of fibrous dust from products made of alumino silicate RCF to humans at EIGA member sites is limited to infrequent maintenance periods only, during which the highest level risk management methods are currently employed to adequately limit exposure to dusts.
- It should not be considered that replacing one insulation material with an apparently similar one is trivial and therefore makes any change straightforward. TRGS 619², 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. Applications can be very different even in the same industrial sector. The evaluation of the feasibility to substitute needs to be done case by case. 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. Finally, field tests should confirm the adequacy of the alternative. Furthermore, any change will involve considerable cost and should only be enforced where alternatives are well proven, technically safe and economically feasible.
- AES wools do not have similar physical and chemical properties compared to alumino silicate RCF (ASW) for high temperature applications. In particular they will not withstand in furnaces with reducing atmosphere with flue gas temperatures of more than 800°C such as steam methane reforming – SMR).
- Since RCF are classified as a Category 2 carcinogen by the European Commission (EC), specific restrictions are imposed on the handling, use, and disposal of RCF in accordance with multiple Commission Directives (European Directives 97/69/EC).

Achieved environmental benefits

Increased lifetime of refractory, reduced waste and human exposure potential.

Cross-media effects

None.

Operational Data

As above.

² See TRGS 619: Substitute materials for alumino silicate wools products published by the BAuA in Germany www.baua.de in German, English and French.

11. Environmental Management Systems

Description

The essential elements of an environmental management system are described in many sources. A summary for the industrial gases industry is found in EIGA document Doc.107 Guidelines on Environmental Management Systems [33], which provides a guide to implementation of an environmental management system according to EN ISO 14001 [34] into the existing quality system according to EN ISO 9001 [35].

EIGA document 122 Environmental Impact of a Hydrogen production plant[6] identifies specific important environmental aspects and impacts to be identified and managed in operation and guidelines for so doing including:

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

Additional guidance is provided in EIGA document Doc.88 Best Environmental Management Practices [27].

Achieved environmental benefits

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

12. Process improvements and plant revamps

Description

As plant and equipment ages plant and especially after around 20 years of plant life improvements and revamps to improve efficiency become more economical. 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). After 15-20 years of plant life, items that should be considered for plant revamps are

- Replacement of burners with improved/ lower NOX types (see section 6.1).
- 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.
- Boiler or cooling water system improvements.

Achieved environmental benefits

Energy efficiency improvements, capacity increases.

NOx 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 <20 years old.

Driving force for implementation

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

Reference literature

Ammonia BREF [12].

13. References

1. EIPPCB Technical Working Group, *Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries*. 2003.
2. European Parliament and of the Council, *Council Directive 2008/1/EC of 15 January 2008 concerning integrated pollution prevention and control 2008*.
- 2bis. European Parliament and of the Council, *Council Directive 2010/75/EU of 24 November 2010 on Industrial emissions (integrated pollution and prevention control)*
3. Dennis Vauk, et al., *Hydrogen Choices*. Hydrocarbon Engineering, 2008(July): p. 83-90.
4. Nazim Z. Muradov, *Production of Hydrogen from Hydrocarbons*, in *Hydrogen Fuel: Production, Transport and Storage*, R.B. Gupta, Editor. 2009, CRC Press: Boca Raton, FL. p. 33-101.
5. J.R. Rostrup-Nielsen, *Production of Synthesis Gas*. Catalysis Today, 1993. **18**: p. 305-324.
6. The European Industrial Gases Association, Doc 122 *Environmental Impacts of Hydrogen Plants*. January 2004: Brussels, Belgium.
7. Walter H. Scholz, *Processes for industrial production of hydrogen and associated environmental effects*. Gas Separation and Purification, 1993. **7**(3): p. 131-139.
8. Sandra Winter Madsen, et al. *Advanced Reforming Technologies for Synthesis Gas Production*. in *International Symposium on Large Chemical Plants*. 1998. Antwerp, Belgium.
9. The European Industrial Gases Association, PP-21 *EIGA proposed amendments to the Greenhouse Gas Emissions Trading Directive*. September 2008: Brussels, Belgium.
10. Charles E. Baukal, *The John Zink Combustion Handbook*. 2001, Boca Raton, FL: CRC Press.
11. EIPPCB Technical Working Group, *Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques for Large Combustion Plants*. 2006.
12. EIPPCB Technical Working Group, *Integrated Pollution Prevention and Control Reference Document on Energy Efficiency*. 2007.
13. European Parliament and of the Council, *Directive 2001/80/EC of the European Parliament and of the Council of 23 October 2001 on the limitation of emissions of certain pollutants into the air from large combustion plants*. 2003.
14. European Committee For Standardization, EN 15259 *Air quality — Measurement of stationary source emissions — Requirements for measurement sections and sites and for the measurement objective, plan and report*. 2007: Brussels, Belgium
15. EIPPCB Technical Working Group, *Integrated Pollution Prevention and Control Reference Document on the General Principles of Monitoring*. 2003.
16. Liz Greenland, *Horizontal Guidance for Noise Part 1 - Regulation and Permitting*. 2002, Environment Agency Commercial Policy Unit.

17. Lesley Ormerod, *Horizontal Guidance for Noise Part 2 - Noise Assessment and Control*. 2002, Environment Agency Commercial Policy Unit.
18. Bundesministerium für Umwelt, *Sechste Allgemeine Verwaltungsvorschrift zum Bundes-Immissionsschutzgesetz (Technische Anleitung zum Schutz gegen Lärm - TA Lärm)*. August 1998.
19. The European Industrial Gases Association, *Doc 85 Noise Management For the Industrial Gases Industry*. January 2002: Brussels, Belgium.
20. J.R. Rostrup-Nielsen, *Catalytic Steam Reforming, Catalysis, Science and Technology*, J.R. Anderson and M. Boudart, Editors. 1984, Springer: Berlin. p. 1.
21. Rickard Vannby and Charlotte Stub Nielsen. *Operating Experience in Advanced Steam Reforming*. in *Large Chemical Plants*. 1992. Antwerp, Belgium.
22. B.M. Tindall and D.L. King, *Designing Steam Reformers for Hydrogen Production*. Hydrocarbon Processing, 1994(July).
23. N. Schumacher, et al., *Trends in low-temperature water-gas shift reactivity on transition metals*. Journal of Catalysis, 2005. **229**(2): p. 265-275.
24. EIPPCB Technical Working Group, *Integrated Pollution Prevention and Control (IPPC) Reference Document on the application of Best Available Techniques in Common Waste Water and Waste Gas Treatment*. 2003.
25. GE Water & Process Technologies, *Handbook of Industrial Water Treatment*. 2009.
26. VGB Powertech Service GmbH, *Guidelines for Feed Water, Boiler Water and Steam Quality for Power Plants Industrial Plants*. 2004
27. The European Industrial Gases Association, *Doc 88 Good Environmental Practices for the Industrial Gas Industry*. January 2008: Brussels, Belgium.
28. ASME, *Consensus Operating Practices for Control of Feedwater/ Boiler Water Chemistry in Modern Industrial Boilers*. 1994, New York, NY: ASME.
29. EIPPCB Technical Working Group, *Integrated Pollution Prevention and Control (IPPC) Reference Document on the application of Best Available Techniques to Industrial Cooling Systems*. 2001.
30. The European Industrial Gases Association, *Doc 122 Environmental Impacts of Hydrogen Plants*. January 2004: Brussels, Belgium.
31. European Commission, *COMMISSION DECISION of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste*. 2000.
32. The European Industrial Gases Association, *Doc.88 Good Environmental Practices for the Industrial Gas Industry*. January 2008: Brussels, Belgium.
33. The European Industrial Gases Association, *Doc 107 Guidelines on Environmental Management Systems*. 2003: Brussels, Belgium.
34. International Organization for Standardization, *ISO 14001:2004 Environmental management systems -- Requirements with guidance for use*. 2004
35. International Organization for Standardization, *ISO 9001:2008 Quality management systems - Requirements*. 2008
36. Sema and Sofres (1991), '*Technical note on best available technologies to reduce emissions of pollutants into the air from the refining industry*. Application of articles 7 & 13 of the Directive 84/360 EEC' report made for European Commission, 135 pgs.
37. The European Industrial Gases Association, *Doc.155 Best available techniques for hydrogen production by steam methane reforming*, 2009.
38. European IPPC Bureau (EIPPCB), *Refining of Mineral Oil and Gas BREF (BAT reference document), final draft July 2013*.

- 39 Overall Plant Performance Testing Standard – ASME PTC 46
- 40 The Babcock & Wilcox Company. *Steam: its generation and use*. The Babcock & Wilcox Company. pp. 34–13. ISBN 0-9634570-1-2.
- 41 Duo et al., 1992 Can. J. Chem. Engng, **70**, 1014-1020