SAFETY OF HYDROGEN, HYCO PRODUCTION AND CARBON CAPTURE

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Prepared by WG-14 Hydrogen Production

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1 Introduction

The purpose of this publication is to provide a summary of operating risks, recommendations and guidelines for the safe design and operations of various hydrogen (H_2), carbon monoxide (CO) and syngas (H_2 & CO) production facilities including carbon (CO_2) capture, sometimes known as HyCO plants.

The HyCO production industry is undergoing a period of rapid expansion and diversification with many newcomers; this document intends to provide a general overview on safety aspects of HyCO production.

1.1 Scope

The scope of this publication covers H_2, CO and syngas production installations and equipment. This publication also covers H_2 production using electrolysers, ammonia (NH_3) dissociation, and carbon capture (CC). It is applicable for the production facility, storage, pipeline distribution systems and trailer filling systems for both gaseous and liquid H_2 and CO products.

The main areas covered in this publication are:

- Facility design safety, including facility siting
- Operational safety
- Product safety and product quality

This document does not cover:

- Any specifics related to road transport
- Cylinder filling facilities
- CO_2 compression, liquefaction, or sequestration after CO_2 capture
- Detailed facility or plant design and specification
- Customer installations.

1.2 Purpose

This publication is intended to provide guidance on best practices for the safe production of H_2, including co-produced CO and syngas, while also considering aspects of carbon capture. It is written in a way to be understood by all, including newcomers to the industry.

2 Definitions

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

2.1 Publication terminology

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

Should: Indicates that a procedure is recommended.

May: Indicates that the procedure is optional.

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

Can: Indicates a possibility or ability.

2.2 Technical definitions

Fugitive Emissions: Leaks and other diffused emissions of gases or vapours from a pressurised containment, from normal operating equipment without defects.

HyCO: In this publication, the term HyCO is used for the production process for any or all of the products Hydrogen (H_2), Carbon Monoxide (CO) and / or syngas.

Liquid Hydrogen (LHy): Also known as LH_2, liquid hydrogen is simply H_2 in its cryogenic liquid state.

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

Syngas: A mixture of H_2 & CO in varying ratios typically after the reactor section of reformer or POx (Partial Oxidation) Sometimes also called oxo gas as a product when the H_2 & CO ratio is fixed.

3 Physical characteristics

Hydrogen is a light (it is the lightest in the periodic table), highly flammable, colourless, odourless, nontoxic, chemical element. At ambient conditions it is in gas phase as a diatomic pair of atoms, H_2. H_2 has a wide range of flammability i.e. H_2 is flammable at most concentrations (in air at typical ambient conditions from 4% to 74.5%) and minimum required energy of ignition is very low (0.02 millijoule, at least ten times lower than that of hydrocarbons like methane or propane). This ignition energy is so low that sometimes autoignition can occur, at high velocities, venting or depressurisations. The auto-ignition temperature of H_2 at atmospheric pressure is 535°C. H_2 burns with an invisible flame in daylight.

Liquid Hydrogen (LHy) exists only at extremely low temperatures, at atmospheric pressure its melting point is -259.3 °C and boiling point is -252.9 °C. LHy is a colourless, odourless liquid with a density at boiling point and atmospheric pressure of 70.8 kg/m3.

Carbon Monoxide is a colourless, odourless, flammable, toxic gas. Like hydrogen, it cannot be detected by the senses. Carbon monoxide is a chemical asphyxiant and acts toxically by combining with the haemoglobin of the red blood cells. Inhalations of high concentrations can cause a sudden collapse without warning.

Like hydrogen, carbon monoxide is flammable over a wide range of mixture ratios (in air typical ambient conditions from 12.5% to 74%. The auto-ignition temperature of CO at atmospheric pressure is 650°C.

Carbon dioxide (CO_2) occurs naturally in Earth's atmosphere as a trace gas, it is an acidic colourless gas with a density about 53% higher than that of dry air. Carbon dioxide molecules consist of a carbon atom covalently double bonded to two oxygen atoms.

4 General safety concerns

Industrial scale HyCO production applies to SMR (Steam Methane Reforming), ATR (Autothermal Reactor) and POx (Partial Oxidation) technology. The feedstocks for such HyCO plants can be a variety of hydrocarbons and ammonia or methanol. These colourless gases or liquids are flammable and/or toxic. These processes are operated at high temperatures (above 800 °C) and H_2 product pressures (usually above 15 barg) while also the H_2 product may be supplied directly from the production plant to the customer often via pipeline systems, typically above 15 barg.

Electrolyser units are used for smaller hydrogen production capacities although recently are also considered and developed for larger hydrogen production capacities (several kNm^3/h). They use power and water as feedstock, however safety aspects related to hydrogen (flammable gas at elevated pressures) are also applicable for such processes.

Some customers who are consuming smaller hydrogen quantities are supplied via hydrogen gas trailers, or gas cylinders. Here hydrogen product is compressed above 200 barg, filled into hydrogen truck trailers or gas cylinders and then transported via public roads to the consumers.

Liquid Hydrogen is produced to supply consumers that require very high purity product, like electronics manufacturers, or where very long transportation distances make it more economical to supply liquid rather than gaseous hydrogen.

Various hazards to personnel or environment associated with hydrogen plant operation need to be addressed and appropriate safeguards to minimise these hazards need to be implemented. Serious hazards to personnel include exposure to toxic releases, fire or explosion, asphyxiation, burns, electric shock and noise.

Safeguards and good practices related to safety, health and environment need to be addressed when designing, operating, and maintaining HyCO plants, more detail is provided in subsequent sections of this document, as a summary:

a. Process
- Mandatory design principles for hydrogen plants based on industrial standards, norms, and regulations
- Material selection
- Pressure / temperature design and safeguarding (pressure systems regulations)
- Plant leak tightness (to avoid flammable / toxic gas releases)
- Positive isolation
- HAZOP (Hazard and Operability Study)
- QRA (Quantitative Risk Assessment)
- SIS (Safety Instrumented Systems)/ SIF (Safety Instrumented Functions)
- Qualified (certified) vendors for all safety relevant equipment
- Blow-down and flare system or vents to safe location
- Toxic and flammable gas detectors
- Fire detectors
- Explosion (hazardous) zones and use of adequate equipment
- PSSR (Pre-Start-up Safety Reviews)
- Continuous purge in flare and vent systems
- Oxygen safety aspects (cleanliness requirements, metallic / non-metallic selection; avoidance of leaks of H_2 into O_2 or vice versa, etc.)

b. Operation & Maintenance
- Maintenance and operation procedures (best practices, standard maintenance, and operation practices etc.)
- Management of Change process (MOC)
- Permit to work process (PTW)
- Emergency response procedures (ERP)
- Document revision control
- Maintenance regime (preventative maintenance, risk-based inspection program, etc.)
- Periodic testing of safety relevant equipment
- Plant and process monitoring
- Training of plant personnel including emergency response personnel
- Plant access control
- Communication systems

c. Personnel Safety

Use of Personal Protection Equipment (PPE); shall adhere to applicable regulatory standards (EIGA DOC 136).

PPE should include:
- safety glasses with rigid side shields
- hard hats
- flame resistant clothing (FRC)
- hearing protection
- safety shoes

– gloves and
– portable personal gas monitors.

- Training program for HyCO safety in addition to general training (hazard awareness including familiarity with safety data sheets, hydrogen production process steps, O_2 safety, operating & maintenance procedures, product safety, personal safe behaviour etc).

d. Hydrogen Tube Trailer Filling - Additional Aspects

- Filling procedures to cope with Joule Thomson effect of hydrogen (warming up during compression / filling)
- Separated trailer stations (outside Ex- and blast zones) with adequate protection between them such as walls or adequate spacing
- Filling bays with individual fire detection with optional extinguisher systems as required by local regulations or company standards
- Trailer grounding connections with optional permissive to allow loading
- Immobiliser system for truck (when coupled to filling system, to avoid towaway incidents)

Above mentioned elements are examples of safeguards to minimise hazards and improve safety of hydrogen facilities.

It is legally required and good practice to install signs stating the potential hazards (e.g. heat, fire, toxicity, asphyxiation, restricted area, etc.) at the access points to the HyCO production unit and in other hazardous areas to alert personnel.

Personnel who are exposed to these areas shall be trained in the risks and shall wear adequate PPE to mitigate potential hazards.

Explanations to some general hazards which are common in all HyCO units are summarised as follows:

a. Toxic release

The fuel gases, the combustion gases (flue gas) and the generated syngas (downstream reformer, POx, or ATR) contain toxic molecules such as carbon monoxide; in case of leakage to the atmosphere the operator can be affected. In areas where a toxic release is possible, portable personal gas monitors should be used.
Procedures shall exist to address the response and corresponding mitigation of a toxic gas release.

b. Flammable gas release

A leaking system (valve, flange, gasket etc) in the plant can cause a flammable gas mixture to develop. This may lead to an energy release and cause significant damage and personnel injury.
In areas where a flammable gas release is possible, portable personal gas monitors should be used.
Procedures shall exist to address the response and corresponding mitigation of a fire or uncontrolled energy release.
An atmospheric vent may ignite when hydrogen is vented. This can be caused by static ignition (e.g. thunderstorm or special weather conditions), by rust particles (also static ignition). Usually, such atmospheric vent systems are equipped with a continuous nitrogen purge to avoid such ignitions or if such purge is not feasible, they are designed to resist a backward ignition into the vent system ("shock pressure resistant"). In such case the atmospheric vent may be equipped with a connection to extinguish the fire after the ignition (e.g. injection of nitrogen or steam).

c. Asphyxiation/Anoxia

Asphyxiation can occur in any confined area or insufficiently ventilated location where air is (partially) replaced by another gas (typically N2, CO2, syngas, NG…); danger begins when oxygen content is less than 19.5% in the air (normal content being approximately 21% by mole or volume).
This potential hazard can exist e.g.
- in reformer penthouses during start up when nitrogen flows through the tubes and can leak.
- in machine houses or other confined areas
- In analyser rooms, where various gases are applied as sampled gas or calibration gas

d. Exposure to hot or cold gases

Combustion gases as well as syngas downstream the reaction process (SMR, ATR, POx) are very hot and can cause burns, therefore personal protection such as cladding, access restriction or proper personal protective equipment (PPE) should be worn when there is a potential of being exposed to these gases or to the hot surfaces of the respective equipment containing such gases. Limit time spent in such areas of the plant.

e. Exposure to Noise

Some areas (e.g. reformer, PSA unit, compressors, pumps, utilities as cooling tower, etc) in the HyCO production unit can expose personnel to high noise levels. Personnel should be aware of the cumulative effects of working in a high noise environment. These effects can include irreversible damage to the ear or additional fatigue that can lead to accidents.
A noise level survey should be completed and shall meet regional regulatory requirements. Hearing protection requirements shall, as a minimum, meet regional regulations.

f. Oxygen Hazards
O2 enrichment and oxygen safety aspects as described in EIGA Document 13 - Oxygen Pipeline and Piping Systems.

Reference is made to:
EIGA DOC 15: Gaseous Hydrogen Pipelines [1]
EIGA DOC 172: Combustion Safety for Steam Reformer Operation [2]
EIGA DOC 136: Selection of Personnel Protective Equipment [3]
EIGA DOC 13: Oxygen Pipeline and Piping System [4]

5 Safety Considerations Relating to HyCO Plant Design

Safety needs to be considered early in the plant design phase to ensure safety and the health of the public, plant personnel, contractors, and end user. A plant should be designed to minimise the risks and environmental impact through the whole plant life cycle.

A Health Safety and Environmental (HSE) plan ensures that HSE requirements are correctly defined and implemented.

The HSE plan ensures that all applicable laws, standards, and guidelines are considered. If not mandated by law, assignment of a dedicated HSE specialist is good industrial practice.

5.1 Design safety process

5.1.1 Design safety in conceptual, basic, and detailed engineering design stages

The terms conceptual, basic, and detailed engineering are commonly used in industry; however, the allocation of activities and content of these engineering phases may differ between companies. The following is given as an example of typical workflow.

A key activity in the **conceptual stage** will be the Hazard Identification study (HAZID) to identify the potential hazards, reduce the probability, and mitigate the consequences of an incident. HAZID is used both as part of a Quantitative Risk Assessment (QRA) or as a standalone analysis for example in installation, modification, replacement, or debottlenecking.

During the **basic engineering** stage, the requirements for the plant design are further refined. The mandatory codes and standards for HyCO facilities will vary by location. Correct identification of the applicable standards and codes per engineering discipline is critical for successful completion of the plant design considering all the safety aspects.

During the basic engineering stage, a loss prevention philosophy may be documented by means of various engineering deliverables, not limited to:

- Active and passive fire protection plan (including fire and gas detection philosophy)
- Emergency isolation and depressurization plan
- Isolation philosophy for maintenance
- Flaring and blow down philosophy
- Effluent and emissions philosophy
- Ventilation concept for enclosed areas (e.g. machine houses)
- Explosion protection concept (hazardous area definition)
- Combustion safety concept

Key for successful implementation of the design safety process in all execution phases is to involve construction and commissioning subject matter experts in the various design reviews as early as the basic engineering stage.

During the **engineering** stage, a key activity will be the Hazard and Operability study (HAZOP). This is a systematic review of the process and operation to determine whether deviations from the design or operational intent can lead to undesirable consequences. Potential causes and consequences of the deviation as well as existing safeguards are documented, and safeguards are confirmed, or mitigation actions are planned. The HAZOP can impose the need for further detailed studies such as Layers of Protection Analysis (LOPA) and Safety Integrity Level quantification (SIL).
Tie-ins with off-site feed or product transfer likely require a dedicated and separate interface HAZOP.

Other studies such as Failure Mode and Effect Analysis (FMEA) can be applied, depending on the status of the project and the actual inventories of hydrogen handled.

In detailed engineering, all the requirements set forth in the planning documents shall be processed into material and equipment specifications, piping, and instrumentation diagrams (P&IDs), construction drawings and operating and maintenance procedures.

The project should have a Management of Change (MOC) procedure in place to document and approve any variances to the basic engineering plan if design parameters change. A special focus must be given to any changes which impact the HAZOP.

During the detailed engineering stage all action items defined in the HAZOP or other studies should be completed and their closeout documented.

Besides the drawings for construction, the following documents are generated during the engineering phase, these enable completion of the safety critical scope such as:

- Safety Valve list
- SIS documentation including SIL loop trip and alarm setting list
- Emergency Shutdown procedure
- Grounding Design and Procedures
- Material Safety datasheets
- Fire and gas detection plan
- Spill containment philosophy
- Construction safety plan
- Safety Signs and labelling list

5.1.2 Design safety in Project construction

Design safety is also a fundamental part of construction. Aspects which need to be considered include, not limited to:

- Late imposed design changes causing unplanned workarounds
- Coordination between different construction sub-systems or trades

- Maintenance access
- Manageable loads during construction
- Trip and fall prevention
- Works at height
- Confined spaces
- Hazards introduced by adjacent facilities

Construction punching should take place in an organised way. The various subsystem punch lists should clearly prioritise safety critical points so they can be resolved prior to subsystem handover.

5.1.3 Design safety in Project pre-commissioning then commissioning

Before any commissioning activities begin, all design documentation should have been issued with approved for commissioning status.

Handover of subsystems from construction to commissioning will take place in a controlled and documented way by means of a turnover system initiated in the construction phase.

Typically, prior to first energization or introduction of process fluids the project HSE representative or his/her designee will confirm:

- Documented completion of all safety related construction punch list items.
- Verification of as built installation with P&ID.
- Completion of all HAZOP and other safety study action items.
- Correct installation of safety critical systems such a safety valves and safety instrumented functions.

Any deviations to the design documents will be assessed through the formal MOC process prior to commissioning. The MOC process will include updating and reissue of the safety critical design documents.

5.1.4 Design safety in Project closeout

For safe operation of the facilities any changes introduced during construction and commissioning are captured in the design documents and incorporated into the ‘as built’ set of drawings and documents. Typical critical drawings for future safe operations of a unit can be, not limited to:

- Safety valve list and calibration records
- Pressure vessel specifications
- Line list as built
- P&ID as built
- Civil and infrastructure drawings, particularly for underground services
- Electrical drawings, protection relay settings record
- Critical instruments calibration records
- Logic, including trip settings, jumper log and recorded verification of interlock and shutdown systems.

5.2 HyCO specific engineering and design guidelines

This section provides a summary of guidelines and best practices for a safe design of HyCO facilities. Several EIGA publications are available with more in-depth information on the various topics handled in this section.

5.2.1 Facility siting and equipment lay-out

The selection of the plant location and the equipment lay-out shall consider industrial facilities and residences located in the surrounding area and the on-site usage of flammable materials.
Equipment spacing shall consider the requirements of the plant fire-water protection system, maintenance requirements, and the electrical hazardous area classification.

To determine a plant lay-out with sufficient safety distance the design team shall consider the following, non-limitative, list of attention points:

- Distance between major groups of process equipment for fire containment and firefighting.
- Inventory planning of hazardous products.
- Compliance with local rules and regulations
- Safe distance to plant fence or plant roads and public roads.
- Distance of flammable gas process installations to open ignition sources or equipment with high surface temperature.
- Control rooms, labs, workshops, or other facilities regularly housing personnel should be located on the periphery of the unit.
- For facilities considering storage of hazardous liquid gases such as Liquid CO or H_2, a detailed risk assessment is required, including the definition of potential spill scenarios and their dispersion analysis.
- Distance (location and height) of vent and flare stacks respective to nearby occupied buildings, elevated structures, platforms, and any overhead power lines, to mitigate damage, asphyxiation risk and to ensure radiation and remains below hazardous levels.
- External blast load on occupied buildings to determine a safe location, or the need for blast resistant design.
- Noise should be limited or attenuated to below local limits, so as not to pose a hazard or nuisance to local populations or plant personnel. This applies to continuous sources of noise such as compressors, also intermittent noise such as PSA de-press venting.
- Design of roads, truck and trailer loading bays and parking facilities to ensure safe personnel walkways and mitigate the risk for collision incidents with critical utilities, process or storage equipment.

Reference is made to:
EIGA DOC 15 Hydrogen Facilities [1]
EIGA DOC. 187 The Location of Occupied Buildings in Industrial Gas Plants [5]
EIGA DOC. 75 Determination of Safety Distances [6]
EIGA DOC 122 Environmental Impacts of Hydrogen Plants [7]
EIGA DOC 154 Safe Location of Oxygen and Inert Gas Venting [8]

Typically, specific software tools are applied to support process hazard analysis:

- Analyse situations that present potential hazards to life, property, and the environment and to quantify their severity. Consequences may then be managed or reduced by design of the process or plant, modification to existing operational procedures, or by implementing other mitigation measures.
- Illustration of the outcomes that may result from the hazards on site.
- Assist in compliance with safety regulations.
- Enable more effective response to hazardous incidents by understanding their outcomes.
- Assure safe plant and process design.
- Provide input to safety studies to be performed later in the design process.

The Seveso Directive can apply to larger facilities - The SEVESO principles:

- The Seveso-III-Directive (2012/18/EU) aims at the prevention of major accidents and mitigation of the consequences of accidents involving dangerous substances.
- The Directive covers facilities where dangerous substances are present (e.g. during processing or storage) in quantities exceeding certain threshold. Excluded from the Directive are certain industrial activities which are subject to other legislation providing a similar level of protection (e.g. nuclear establishments or the transport of dangerous substances).
- Depending on the quantity of dangerous substances present, facilities are categorised into lower and upper tier, the latter are subject to more stringent requirements.

- The legal framework established by the Directive creates a continuous improvement cycle of prevention, preparedness, and response to major accidents. The cycle is closed by provisions on lesson learning.

Reference is made to:
EIGA DOC 60 – Seveso Documents [9]
Seveso-III-Directive (2012/18/EU) [10]

5.2.2 EU directives relevant for Hydrogen Facilities

The following, non-limitative, summary of EU directives is applicable for HyCO facility safe design:

ATEX 137A directive 99/92/EC defines minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres (ATEX).

ATEX 114 directive 2014/34/EU applies to equipment and protective systems intended for use in potentially explosive atmospheres. It also applies to controlling devices and regulating devices intended for use outside potentially explosive atmospheres but required for or contributing to the safe functioning of equipment and protective systems concerning the risks of explosion.

The PED (Pressure Equipment Directive – 97/23/EC & Pressure vessel directive: 2014/68/EU, as amended) applies to the design, manufacturing, and evaluation of CE conformity of pressurised equipment or set of equipment that work under a pressure above 0.5 barg.

Machinery directive: 2006/42/EC applies to machinery.

Low voltage directive: 2014/35/EU For the purposes of this directive "electrical equipment" means any equipment designed for use with a voltage rating of between 50 and 1000 Volt for alternating current and between 75 and 1500 Volt for direct current.

Electromagnetic compatibility directive: 2014/30/EU applies to apparatus liable to cause electromagnetic disturbance or the performance of which is liable to be affected by such disturbance. It defines the protection requirements and inspection procedures relating thereto.

Reference is made to:
ATEX 137A Directive 99/92/EC [11]
ATEX 114 Directive 2014/34/EU [12]
Pressure Equipment Directive 97/23/EC [13]
Pressure Vessel Directive 2014/68/EU [14]
Machinery Directive 2006/42/EC [15]
Low Voltage Directive 2014/35/EU [16]
Electromagnetic Compatibility Directive 2014/30/EU [17]
EIGA DOC 134 Potentially Explosive Atmospheres EU Directive 1999/92/EC [18]

5.2.3 Global Standards Relevant for HyCO Plants

The following, non-limitative, summary of standards is applicable for HyCO facilities and issued by global standardization bodies (ISO, IEC):

ISO/TR 15916:2015. Basic considerations for the safety of hydrogen systems [19]

ISO/TS 19883:2017. Safety of pressure swing adsorption systems for hydrogen separation and purification [20]

IEC EN 60079-10 "Electrical apparatus for explosive gas atmospheres. Classification of hazardous areas" [21]

IEC/EN 60079-14 "Electrical apparatus for explosive gas atmospheres. Classification of hazardous areas" [22]

5.2.4 Spill control

Containment of potential spill sources such as naphtha and heavier hydrocarbons, plus machinery lubricating oil, wastewater and runoff, amines for CO_2 removal systems and products such as liquid H_2 and CO shall be considered. When siting a plant, site specific consideration should be given to the possibility of the movement of vapour clouds, originating from spillage or venting; in addition, wind direction and the topography shall be considered.

For underground installations, additional requirements should be considered.

Heavier than air hydrocarbons can accumulate in a low-lying confined space i.e. a pit, drain or underground room. The dispersion of these heavier than air gases can go surprisingly long distances if channelled in ducts or pipes. As a guide no openings to low lying confined areas should be allowed within 10m of the storage of heavier than air flammable gases. Underground sewers should be equipped with water seals to avoid gases migrating to other areas.

Liquid hydrogen, spilled to the atmosphere evaporates rapidly. One litre of liquid hydrogen gives approximately 850 litres of gaseous hydrogen at ambient conditions. Therefore liquid hydrogen storage installations should generally be situated outdoors. A LHy storage should not be located beneath or adjacent electric power cables, piping containing other hazardous materials. Concrete paving should be installed at potential spill locations.

Dykes, bunds or diversion kerbs or gradients should be used to ensure that any liquid leakage is limited from spreading and impacting other plant areas.

Reference is made to:
EIGA DOC 06 Safety in Storage, Handling and Distribution of Liquid Hydrogen [23]
EIGA DOC 171, Storage of Hydrogen in Systems Located Underground [24]

5.2.5 Building design

All buildings and enclosures containing process equipment or gas storage shall maintain a safe atmosphere. This is applicable for occupied buildings but also non-occupied buildings such as machinery buildings or analyser enclosures.
Typical measures to accomplish and maintain a safe atmosphere are:

- Roof areas shall be designed to avoid accumulation of hydrogen.
- Enclosures shall be equipped with atmospheric monitors for detection of oxygen deficient or enriched atmospheres and gas monitors.
- Adequate ventilation system shall be provided.
- Automatic activated high-volume ventilation may be applied in case of detected unsafe condition.
- Ventilation openings shall not be installed where they can pull in hazardous gases.
- Process equipment should be shut down in case of detected unsafe condition.
- Upon detecting of an unsafe condition, a visible alert and audible alert shall be activated. A system test button should be located at all primary entrance(s) to the monitored space.

Reference is made to:
EIGA DOC 215: HyCO Plant Gas Leak Detection and Response Practices [25]

A safety study should determine the external blast load on occupied buildings. Bursting pressure vessel (BPV) and vapor cloud explosions (VCE) may be credible explosion scenarios associated with the hydrogen of carbon monoxide production unit. The study will calculate the anticipated load applied to the building from a blast wave. A Blast-resistant building is designed to withstand this load and protect the people, equipment, and assets inside of the building.

A safety study may also define the need to incorporate a specialised HVAC system for occupied buildings, to maintain positive air pressure and isolate the building from external hazardous ambient conditions.

5.2.6 Fire Protection and Prevention Systems

The facility fire protection system shall, as a minimum, meet the requirements of the relevant authority. As part of the loss prevention philosophy, part of the design safety plan, the requirements for fire water protection systems should be determined.

Typically, in the conceptual stage of a project the local authorities such a fire department and subject matter experts are consulted and can advise on the application of:

- Firewater flow, source, and any redundancy requirements
- Hydrants and automated or manual monitors, capacity, range, and location
- Hose reels/cabinets and their location
- Hand fire extinguishers, properties, and location
- Deluge and sprinkler systems
- Application of fireproofing on structures to avoid domino effects in case of structural collapse.

The physical properties of hydrogen particularly at high pressures can make the length of the dispersion (and the potential jet flame) from a small hole (10mm or less) greater than that for other gases. Hydrogen fires are virtually invisible to the naked eye. If there is suspicion of a hydrogen jet flame, then care shall be taken in approaching the area. The flame may be impacting other equipment leading to overheating and potential loss of containment. The flame may be horizontal and present a high temperature cutting risk.

Every H_2 and HyCO plant should be equipped with a fire detection and alarm system, typically thermal, UV, IR and/or smoke detectors that alert the plant operator. Requirements for the fire alarm system are typically suggested by the project team and confirmed by process safety and shall follow local authority requirements. Minimum requirements may also need to be agreed with insurance providers.

5.2.7 Plant Emergency Shutdown

Every H_2 and HyCO plant should always remain in a safe condition, defined as the safe operating envelope, and any move beyond safe limits (typically defined in an alarm and trip list) shall trigger an alarm, and then if not corrected, an automatic trip, which will bring the plant back to a safe condition, for example using an emergency shut down system. Larger facilities consisting of several units or satellites can have individual area isolation or trip systems.

For safe shutdown, the following automatic functions could be considered in the design:

- Stop supply of feeds, fuels, products etc.
- Isolate process sections with shut-off valves
- Isolate storages with shut-off valves
- Shutdown compressor and critical rotating equipment

5.2.8 Safe Design Principles for Plant Systems

Specific actions should be taken during the plant design phase to reduce the likelihood of leaks developing within the facility. Proper metallurgy selection and construction methods should be specified to avoid leaks in piping or vessels. Potential leaks can be reduced by reduction of flanged and threaded connections.

The correct valve selection will be based on the design and operating conditions of the valve (temperature, pressure, composition, frequency of valve operation, etc.) as well as any regulations regarding fugitive emissions.

Reference is made to:
EIGA DOC 215 HyCO Plant Gas Leak Detection and Response Practices [25]

Design for safe maintenance – The plant design shall have provisions for physical isolation of control valves, rotating equipment and other equipment which requires service. Since gaseous hydrogen has a very low density, assume a single shut-off valve can leak.

Suitable isolation systems can be:

- Double block and bleed valve system
- Air gapping
- Spectacle or blind
- Combinations of the above

Plant design should consider that flammable gas systems shall be purged with an inert gas such as nitrogen before hydrogen or flammable gases are admitted. All flammable gas systems shall be purged with nitrogen before air is admitted. The purge discharge shall be piped to a safe location. Under no circumstances shall air be purged into an active vent or flare stack.
Purge gas supply and discharge connections should be located to provide a full sweep of the system to be purged, being mindful of fittings such as check valves and back flow, multiple connections and high point vents may be required. Interconnections between the process gas and inert gas / nitrogen purge systems shall be provided with a positive means to prevent the flow of process gas into the nitrogen purge system.

5.2.9 Mechanical Integrity

Profound knowledge about failure mechanisms in metals and alloys is an absolute prerequisite for correct material selection for HyCO facilities and the prevention of safety critical failures.
Together with failure mechanisms, the recognition of service conditions such as temperature, environmental parameters, loading conditions, assembly parameters, and interactions with neighbouring materials and the information pertaining to the industrial production processes involved in the fabrication of the component are of equal importance.

The following failure modes can be applicable for HyCO facilities:

Cyclic pressure fatigue:
Welded H_2 vessels in cyclic pressure service can fail due to initiation and propagation of cracks in welds and in their surrounding heat affected zone. Factors influencing the likelihood of failures include the vessel materials, presence of any weld defects or base metal defects, severity of cyclic service (cycle count and pressure range), design features causing higher local stresses e.g. welded attachments, etc. Vessels in cyclic service typically have an increased inspection requirement, and it is essential that the total lifetime cycle count is considered during design.

Metal dusting:
Metal dusting is a rapid form of carburization that leads to loss of pipe or vessel thickness. This phenomenon occurs in carburizing atmospheres in a combination of temperature, pressure, and composition (i.e. carbon monoxide content).

Thermal aging:
High temperature cast alloys are susceptible to thermal aging where the microstructure changes over time at service temperature. This leads to significant reductions in strength and ductility. The susceptibility to thermal aging strongly depends on the alloy chemistry, temperature, and exposure time. Thermal aging will not lead to failure on its own but will lead to increased creep rate that will ultimately lead to failure.

Thermal fatigue:
Thermal fatigue is the result of cyclic stresses caused by variations in temperature. Cracking can occur anywhere in a metallic component where relative movement or differential expansion is constrained, particularly under repeated thermal cycling.

Creep:
At high temperatures metal components can slowly and continuously deform under load below the yield stress. The time-dependent deformation that occurs under stress is known as creep.

Excessive stress:
Piping systems are designed considering all normal operating conditions. These conditions include internal pressure, temperature, weight, and thermal expansion. Stresses due to these conditions are

kept within the relevant code limits or other more conservative limits established by the designer. Stresses that are higher than the design limits can develop due to improper construction, unexpected behaviour, or improper maintenance of the piping support system.

High temperature hydrogen attack:
High temperature hydrogen attack (HTHA) is function of elevated temperature (>200 C) and H_2 partial pressure (>3.5 bara). At these elevated temperatures H_2 can react with the carbon in steel to cause decarburisation and an overall loss in strength leading to eventual cracking. Some grades of steel are more resistant to HTHA, stainless steels are immune to HTHA attack. Carbon steel is the most susceptible, and alloys including Cr and Mo stabilise carbides thus improving steel resistance. Post-Weld-Heat-Treatment (PWHT) is beneficial in preventing HTHA as it stabilises carbides and reduces residual weld stresses. See API RP941 (Nelson curves) for HTHA.

Hydrogen embrittlement:
Hydrogen embrittlement is the degradation of material properties due to the presence of hydrogen. Hydrogen embrittlement manifests itself as reduction in tensile strength and ductility, accelerated fatigue crack growth, and cracking under sustained load.

Anti-fatigue for H2 PSAs cyclic pressure vessels (EIGA Technical Bulletin 42 Welded Gaseous Storage Vessels and Hydrogen Compatibility).

Impingement velocity curve and metal selection for piping/ equipment in O_2 service (EIGA DOC 13)

Reference is made to:
EIGA Doc 202: Mechanical Integrity of Syngas Outlet Systems [26]
EIGA Doc 210: Hydrogen Pressure Swing Adsorber (PSA) Mechanical Integrity Requirements [27]
EIGA Technical Bulletin 42: Welded Gaseous Storage Vessels and Hydrogen Compatibility [28]
EIGA DOC 13: Oxygen Pipeline and Piping Systems [4]
EIGA DOC 215: HYCO Plant Gas Leak Detection and Response Practices [25]
EIGA DOC 230: Safe Catalyst Handling in HYCO plants [29]
EIGA DOC 238: Prevention of Plant Instrument and Utility Gas System Cross Contamination [30]
API RP941: Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants [31]
NFPA 2: Hydrogen Technologies Code [32]
NFPA 55: Compressed Gases and Cryogenic Fluids Code [33]

5.2.10 Piping systems and in line items

Due to the hazardous nature of the gas in HyCO facilities, above ground pressure containing parts such as piping, valve bodies, strainer, and filter housings, etc. are typically made of metallic materials. The use of non-metallic materials should be limited to services such as valve internals (inserts only), external coatings, special low-pressure services, etc. which do not provide primary mechanical strength.

There are no special velocity restrictions for piping in hydrogen service other than the underlying economics. However, the sonic velocity of hydrogen is approximately four times that of most flammable gases. Therefore, close attention should be paid to possible erosion and abrasion at such items as control valves and relief valves.

Welded connections are preferred, for process lines and should be used wherever practical to minimise potential leak sources, with flanged connections acceptable for maintained equipment such as relief valves. Where welded connections are not practical, flanges are the next best choice. Leak resistant flange types such as raised face, tongue and groove, or ring joint flanges shall be used. Gasket materials shall be appropriate for the design pressures and temperatures and be hydrogen compatible and leak resistant. In addition, consideration should be given to resistance to fire, due to the flammability of hydrogen. The use of brazing should be avoided, also, low melting point metals should be avoided.

Instrument tubing shall be stainless steel with compression fittings. The use of continuous runs shall be maximised to reduce the number of fittings since these can be leak sources.

The major concern specific to pure hydrogen service is to prevent leakage either to the ambient or across the valve. Leakage to ambient is most frequently caused by packing and bonnet leaks and to a lesser extent by leaking castings.

Reference is made to:
EIGA Doc 121 Hydrogen Pipeline Systems [34]

5.2.11 Pressure Swing Adsorber mechanical integrity

Pressure swing adsorption (PSA) exists as the primary method of product purification in most large-scale HyCO production facilities. Mechanical integrity of the vessels, piping, and piping components is crucial to ensure that this equipment is fit for service.

The PSA system is a multiple fixed bed gas purification process that uses materials that selectively adsorb one or more gas species from a mixture. The system is typically comprised of a number of adsorbent vessels that operate in various stages of adsorption and desorption. Purified hydrogen gas is collected in a high-pressure product header. Low pressure contaminant-rich rejection stream is collected in a low-pressure header and sent to the surge drum.

Carbon steel is the typical material of construction for the entire PSA system, although stainless steel is sometimes used for chemical feeds.

Pressure vessels used in a hydrogen PSA are subject to fatigue loading by cyclic pressures. Such vessels shall be designed and constructed in accordance with recognised pressure vessel codes and fatigue design rules.

The number of design cycles for a specified operating pressure range (i.e. P_{max} - P_{min}) is established during the design phase of the vessel when applying the relevant design codes. The number of cycles chosen for the design should be equal to or greater than the expected cycles for the specified operating duration of the vessel.

EIGA publication Doc 210 provides several good engineering design practices for PSAs systems in hydrogen service.

Reference is made to:
EIGA DOC 210: Hydrogen Pressure Swing Adsorber (PSA) Mechanical Integrity Requirements [27]

5.2.12 Safe Emission - Vent Stacks and Flares

The design should consider the required inspection frequency of safety valves, noting that in many regions it is not permitted to include isolations around a safety valve.

Safety valves and other vents which release toxic gases such as syngas containing carbon monoxide should be routed to flares, not vents.

The design of flammable gas vent stacks aims at managing the following three main hazards:
- Deflagration due to delayed ignition of the flammable hydrogen/air mixture coming out of the vent stack.
- Thermal radiation generated at the vent tip, by a potential flame if a vent was to ignite.
- DDT (Deflagration to Detonation Transition) inside the stack due to the acceleration of the combustion of the air/hydrogen mixture that can be present inside the venting system (in the presence of an ignition source). This hazard is relevant if air can enter the venting system.

The design of flares also must manage hazards:
- Deflagration due to delayed ignition through installation of pilot burners
- Accumulation of flammable gases by continuous purging of flare sub-headers and avoidance of dead ends.
- Reverse flow of air, also by continuous purging of flare sub-headers.
- Thermal radiation, by appropriate design, diameter, height and positioning of the flare.

In HyCO production plants the vented gases are frequently wet, so the design should allow for this, for example using sloped lines and knock-out drums to remove free water.

The forces involved during venting can be very high, so careful consideration should be given to piping stress and design of pipe supports.

Safe design of vent and flare systems is a complex engineering and design activity, which should account for several operational and environmental parameters.

For example, reference is made to:
EIGA Doc 211 Hydrogen Vent Systems for Customer Applications [35] which provides engineering and design practices for hydrogen vent systems in customer applications.
EIGA DOC 154: Safe Location of Oxygen and Inert Gas Vents [8]

6 Operational Safety and Maintenance

As H_2 is flammable and has a high tendency to leak, special considerations are necessary to ensure safe operation and maintenance.

6.1 Normal operations

The minimum requirement for normal H_2 production plant operation includes having a safe design, with a well-defined operating envelope. Further considerations include:

- Environmental permits covering limits for environmental impact. Operations shall remain within the limits of a site’s operating permit.
- Hazard detection including flammable gas leak and fire detection; emergency response planning including but not limited to firefighting, evacuation, alerting neighbours, plus coordination with third parties such as emergency responders and the public.
- Facility security including prevention of unauthorised access to the potentially hazardous H_2 production facilities, including robust cyber security to prevent malicious access to control systems.
- Sufficient manning levels for operation and maintenance, aligned with plant design, to enable safe operations, including staff training plans and records.

6.2 Work Permit Systems

A Work Permit System is a formal system used to control work that is potentially hazardous; it is an integral part of safe systems of work for maintenance, construction, and operational activities. It goes beyond the scope of this document to fully define the work permit system, however HyCO production facilities, by their nature, provide challenges for the safe implementation of work.

The work permit system when correctly implemented ensures that risks to people, processes, assets, or the environment are consistently identified and evaluated, and that precautions against injury or damage are implemented, acknowledged, and documented, so that work hazards are mitigated.

HyCO production hazards include highly flammable process fluids at high pressures and temperatures, chemical reactions, toxic hazards (carbon monoxide, catalyst) etc.

In implementing the work permit procedure, a Permit Issuer reviews and assesses the tasks to be carried out, then when satisfied that work has been made safe, issues a Permit-to-Work form which is a standardised document authorising work to take place on an operating plant. The form documents the potential hazards, and their controls. The work permit system supplements normal hazard control methods and does not in itself guarantee that work is safe.

Special considerations that apply to HyCO production, requiring additional controls, include:

- Hot work (cutting, grinding, welding etc.), because of the flammability and low ignition energy of H_2
- Confined space entry (e.g. vessel inspections and catalyst work with a risk of asphyxiation, poisoning, entrapment, and engulfment etc.)
- Catalyst and chemicals handling
- Inert atmospheres e.g. N_2 purges during maintenance
- Controls system bypasses

Safeguards to minimise the risk from HyCO production hazards include:

- Atmospheric testing equipment which should be used to check LEL, O_2 levels and other hazards such as toxic hazards such as CO and H_2S, as applicable.
- Adequate ventilation is required to prevent any build-up of gases.
- Selection and use of suitable personal protective equipment for the hazards at the site, such as overalls manufactured to meet EN11612 for heat and flame resistance, and EN1149-5 for anti-static properties.

Reference is made to:
EN ISO 11612:2015 Protective Clothing – Clothing to Protect Against Heat and Flame [36]
EN 1149-5:2018 Protective Clothing – Electrostatic properties [37]
EIGA DOC 40: Work Permit Systems [38]
EIGA DOC 23.23: Work Permit [39]

6.3 ATEX zoning and compatibility of equipment

All hazardous areas shall restrict access to only authorised, trained personnel.

Beyond the design phase, covered earlier in this document (see section 5.2.2), when operating or maintaining a H_2 facility, the tools and equipment used must be assessed in the work permit and comply with the applicable ATEX zone they will be used in.

During major maintenance it can be possible to de-classify ATEX zones on a production plant after all flammable gas hazards are eliminated, following thorough draining then purging and gas testing procedures. This would need careful procedural controls.

6.4 Management of Change (See also EIGA DOC 51 Management of Change)

Management of Change (MOC), when correctly implemented, ensures that all risks related to health, safety, environmental and particularly to process safety are controlled when changes are made to production facilities; this includes all aspects of their operation and documentation. Any change, permanent or temporary, can potentially affect safety, environmental performance, regulatory and legal compliance, quality, and reliability of a process or system. MOC is used to ensure that all these factors are considered and addressed consistently.

There have been numerous examples from throughout industry where badly implemented modifications to production plants have contributed to incidents, where the failure to properly manage a temporary plant modification was thought to be a cause of the subsequent disaster.

It is key to have a good as-built set of plant documentation as a starting basis (see section 5), including P&IDs, electrical line drawings, piping isometrics, work instructions etc. which must be kept up to date throughout the life cycle of the plant.

Typical changes incurred during the life cycle of a HyCO production plant include equipment upgrades, increased automation, replacement of obsolete or failed components, debottlenecking, or other expansion.

An evaluation of the change should include evaluation of the effect on the plant's HAZOP, which should be a live document that is updated in response to changes.

The MOC process must ensure that suitably experienced approvers are assigned, including Process Safety and all other disciplines as necessary. Approvers must consider the effect of the change on all aspects of operation, which for HyCO production includes (not limited to) ATEX zoning, overpressure relief, materials compatibility, alarm management and alarm response, and fail-safe operating states.

After approval of the MOC, implementation may take place. Care must be taken to avoid any divergence between the changes implemented compared with what was approved.

Prior to close out of the MOC, all associated MOC tasks must be completed, including the update of all plant documentation. A good MOC system also covers communication and training for individuals affected by the changes.

Reference is made to:
EIGA DOC 51: Management of Change [40]

6.5 Isolation and Lockout/Tagout of systems for safe working

A particular hazard associated with HyCO production systems is the tendency of gases to leak, for example across closed valve seats or out to atmosphere via valve packing or piping joints, or by thermal expansion caused by cold to hot changes during start-up.

Whenever performing any work, exposure of personnel to hazardous process fluids or energy sources must be prevented. Systems must be isolated and made safe using the lockout/tagout/try methodology (LOTO).

Potential energy sources prevalent with HyCO production include electrical, pressure, thermal, chemical, gravity, mechanical, for example spring loaded valve actuators, residual pressure in vessels.

Isolation Plan - A typical plan would be cross referenced with the permit-to-work and would include a marked-up P&ID showing the full extent of the system isolations, plus a corresponding valve and blank/blind list indicating required positions.

- All live process systems that may impact the work area must be adequately isolated or disconnected, then de-energised/depressurised, as applicable. Isolation can be performed in several ways. In order of decreasing levels of safety, they are:
  - Physical air gap disconnection of piping
  - Fit blanks/blinds
  - Double block and bleed valves
  - Double valve isolation
  - Single valve isolation (note single valve isolation is not recommended for use in H_2 isolations)
  - Automatic valves
    - Note that actuated valves are not suitable for isolation unless additional precautions have been taken, for example disconnect the air and power supplies, clamp valves in position, check for presence of minimum stops.

- Criteria to consider when choosing isolations include the process fluid including its toxicity and flammability, pressure, temperature, and the system volume behind it; the system design parameters, for example what valves, flanges, spools are available; the effect on personnel and the surrounding area in the event of an isolation failure. Hydrogen, syngas and CO, particularly at higher pressures or more extreme conditions, require a more robust isolation.

- After isolations are put in place, the work site must be further made safe before any work begins:

  - Thoroughly drain at all system low points, then de-pressurise to a safe location.

  - Purge with inert gas until free from hazardous fluids.

  - Open to atmosphere and thoroughly ventilate, alternatively systems can be air purged before opening.

- Some isolation plans may benefit from a formal review, such as those which are complex, or with significant hazards. The following situations may fall into this category: - confined space entries; isolation from highly toxic process fluids; isolation using only single valves, or where control valves are used for isolation.

6.6 Purging and Inerting

When working with HyCO production plant and equipment, owing to the characteristics of the process fluid, it is necessary to prevent a combustible mixture of gaseous fuel and air from forming inside a system during maintenance.

Purging is required when systems have been in service and must be opened to the atmosphere or have been opened to the atmosphere and must be put back into service. Analysers should be used to test the flammable gas concentration and oxygen concentration of the systems when they are purged.

- All depressurising and purging operations must be directed to a safe location. Temporary vent or flare siting should take into consideration location of any adjacent equipment such as process air intakes, buildings, and air conditioning/ventilation systems.

- While any inert gas, for example, nitrogen, argon, helium, but not carbon dioxide, may be used for purging purposes, nitrogen is the gas most likely to be available and economically practical for equipment purging.

- There are two main methods of purging - continuous and pressure pulsing:

  - With continuous purging gas is swept from one end of the system to the other, it is particularly suitable for linear systems with minimal dead legs.

  - Pressure pulsing is suitable for more complex systems or where vents are not available in key places, here the equipment is pressurised with inert gas then vented to a safe location repeatedly until the residual gas is diluted to a safe level.

- A safe target for dilution of flammable gas with inert gas is 25% of LEL, which in the case of H_2 means an absolute value of max 1% H_2 remaining in N_2 before exposing to air.

- Purge gas may not be effective in removing residual hazardous materials from equipment that contains scale, heavy liquids, sludge, or solids. Often it is necessary to heat, steam clean, or wash equipment that has any of these characteristics.

- If there are catalytic reactors in the maintained system, it can be essential to prevent air ingress, to preserve the catalyst by keeping it in the reduced state with N_2.

- To fully purge process gas from trapped pockets within some types of reciprocating machines, rotary compressors or blowers, the machines may need to be manually turned/barred over, while introducing the inert gas.

- If testing using a gas monitor, consider the background gas that the monitor is capable of measuring in. Some monitors are accurate for %LEL in air but not necessarily in inert or other gases.

- After maintenance is complete, further purging with inert gas is needed to remove oxygen in the system to safe levels (typically below 1%) before flammable gas is reintroduced.

- It is essential to prevent backflow of process fluids to the inert gas source.

- For cryogenic H_2 systems, N_2 is unsuitable for purging at such extreme low temperatures thus helium is typically used.

6.7 Leak prevention

As H_2 is a very light molecule it is at higher risk of leaking out of process equipment, when compared with heavier flammable gases such as hydrocarbons.

- Fugitive emissions are continual, small leaks via valve packing and pipe joints such as flanges & gaskets. Leaks can be minimised by specifying equipment which is designed and rated for hydrogen duty.

- Ensure valves are specified as suitable for H_2 service considerations e.g. bellows type as these can minimise leakage through the stem packing.

- When reinstating equipment after maintenance, leak test using an inert gas such as N_2 and resolve any leaks found before introducing H_2 at low pressure before increasing pressure gradually, pausing to leak check again at interim points. Some leaks may not become apparent until at higher pressures.

7 Quality & Product Safety

There are various typical quality specifications for hydrogen and mostly these are determined by the end user of the product. Large volume customers like refineries or chemical sites usually have specific requirements while customers supplied by gas trailers or gas cylinders tend to follow generally applied hydrogen grades.

It needs to be noted that depending on feedstock, the specific feedstock composition and the applied hydrogen production process the impurities in the hydrogen product like N_2, H_2O, CO, CO_2, C_nH_m, Ar, O_2 etc will vary. Typically each customer will specify acceptable levels for such impurities, based on their specific needs.

7.1 Typical purities for Hydrogen product

Large volume H_2 customers like refineries or chemical sites have specific requirements and define what impurity levels are acceptable. Typical Hydrogen product specification ranges are 99.0 to 99.99 Vol%. N_2 as main impurity is usually regarded as unwelcome but non-critical inert and may range up to 1 Vol%.

Other impurities like O_2, CO, CO_2, H_2O, and higher hydrocarbons (C_nH_m) are limited individually to ppmv ranges. These impurities typically act as contaminants for the production processes of the large volume H_2 costumers and as such are strictly limited to low ppmv-levels to avoid subsequent damages or unwished performance issues in the production processes of the large volume customers.

For hydrogen products delivered by gas trailers or cylinders purity grades are used. The first digit gives the number of 9's, second digit then gives the subsequent number after the 9's, e.g. 4.5 means minimum 99.995 Vol-% of hydrogen in the product.
Typical hydrogen purity grades for gas trailer or cylinder supplies are ranging from 4.5 to 6.0 meaning 99.995 to 99.9999 Vol.-% purity. The respective impurities (N_2, H_2O, CO, CO_2, C_nH_m, Ar, O_2 etc. show only ppmv ranges.

For food applications EU Reg. 231/2012 as well as EIGA DOCs 125 and 126 shall be considered. Typical grade is 3.0 (99.90 Vol% H_2 purity) with: - N_2: <= 0.07%, O_2: <= 10 ppmv, H_2O: <= 50 ppmv

Reference is made to:
EU Reg. 231/2012 [41]
EIGA DOC 126: Minimum Specifications for Food and Gas Applications [42]
EIGA DOC 125: Hazard Analysis and Critical Control Point (HACCP) [43]
Typical H2 purity grades for hydrogen fuel cell applications reference is made to ISO 14687:2019 [44]

7.2 Typical contaminants in Hydrogen vs. production methods

7.2.1 Steam Reformer

H_2 product from a steam reformer will typically contain N_2 (since it is usually present in the hydrocarbon feed stream), plus CO, CO_2, C_nH_m, H_2O (as a result of the process characteristic). Sulphur compounds are not present in the product because of the need to remove them from the hydrocarbon feed stream before the reforming process.

7.2.2 Partial Oxidation (POx)

Impurities in H_2 product deriving from POx based PSA feed gas is mainly Argon from the Oxygen used in the POx reactor. Impurities like CO and CO_2, and inerts like N_2 are mainly specified and reached with the adequate PSA design. Typical values are CO and CO_2 max 10 ppmv and N_2 typically below 10 - 20 ppmv.
The dominating impurity, or better said inert, becomes the Ar ranging typically between 380ppmv to over 900ppmv.
If it is required to reduce Argon content and raise H_2 purity above 99.7% the PSA recovery rate (efficiency) is reduced which goes hand in hand also with further reduction of CO, CO_2 and N_2 impurities. However due to less efficient PSA operation many customers accept the typical Argon levels.

7.2.3 Auto Thermal Reformers (ATRs)

Similar to the POx process, the impurities present in ATR product are typically Ar, CO, CO_2, CH_4, H_2O, N_2, O_2

7.2.4 Water Electrolysers

Values are valid for AEL and PEM:
Typical impurities are O_2 and H_2O only, in the range of 0.5 – 2ppm vol.
Most vendors use 2ppm as typical guarantee values while few vendors go to max. 5ppm.
Traces of N_2, Ar and CO_2 cannot be fully excluded and are also in the range of 0.5 – 2ppm vol.

7.2.5 Liquid Hydrogen

Owing to the extreme cold temperatures involved in producing LHy, there are very few contaminants which can remain in the LHy product, and typical H_2 purity from a LHy plant is 99.9998% (5.8). Most impurities in gaseous H_2 feed (CO_2, H_2O, CH_4, N_2, O_2, Ar) would solidify in the liquefier, therefore gaseous H_2 must be conditioned to reduce these to very low levels before liquefying. Helium can remain in LHy, albeit at low levels.

LHy exists in two main allotropic forms, para and ortho H_2, with para-H_2 being more stable and less susceptible to boil-off, however there is a conversion efficiency cost of producing para-H_2. Some users may need to store LHy in its cryogenic liquid form for longer durations, so a high proportion of para-H_2 can be essential. Other LHy customers can use gaseous H_2 from boil-off productively, for example in shipping where the H_2 demand may be continuous, so a higher proportion of ortho-H_2 may be acceptable.

7.3 Quality control in HyCO production

Quality control on feedstock goes a long way towards assuring quality control of product, often the feed quality control can be done by the supplier with only periodic checking against the supply spec being required.

Quality control on intermediate process streams is typically only necessary to assure that process is operated in a safe, efficient, and reliable manner.

In-line analysers are installed to alarm and prevent any deviation of the product vs specs. Non-conforming product is managed according with producer procedure, in automatic or manual manner mainly depending on plant attendance (manned or un-manned).

Quality control on the product can be performed continuously on the product stream before point of delivery e.g. for pipeline customers; or can be performed batch-wise e.g. for hydrogen tube trailer deliveries which can be analysed before and after filling, to ensure there is no residual contamination from earlier trailer operations.

7.4 Product Safety

Aside from the various hazards relating to the hydrogen and syngas/CO production processes, for example catalyst and amine hazards (see EIGA DOC 230 Safe Catalyst Handling in HyCO Plants), the following hazards apply to the products, note that CO_2 as a product is not considered because it is out of the scope of this document.

7.4.1 Hydrogen

Hydrogen product safety concerns are mostly related to its physical characteristics: flammability, oxygen displacement, high pressure. The amount of H_2 gas required to produce an asphyxiant atmosphere is well within its flammable range, making fire and explosion the primary hazards associated with H_2 and air mixtures.

Hydrogen shall be kept away from heat, hot surfaces, sparks, open flames, and other ignition sources. In case of leaking gas fire, it is recommended not to extinguish, and preferably stop the leak safely by isolating the source of leaking gas, this is because a hydrogen fire is difficult to extinguish, also by extinguishing a hydrogen fire it may allow a flammable gas cloud to build up.

Customer installations should avoid any confined spaces as far as possible, and all precautions to monitor and prevent oxygen displacement must be put in place.

7.4.2 Carbon Monoxide

CO product safety also has concerns related to its physical characteristics: flammability, oxygen displacement, high pressure, but the most significative risk is related to its acute toxicity.
Breathing CO also at low concentration brings to dizziness, headache, nausea, loss of co-ordination and loss of consciousness resulting in sudden death even.
Lethal concentration to 50% of a test population is 3,760 ppm/1h or 1,300 ppm/4h.
Before any emergency intervention it is mandatory to wear self-contained breathing apparatus (any kind of filtering respiratory protection is useless).
In case of inhalation remove victim to uncontaminated area, keep him/her warm and rested, perform cardiopulmonary resuscitation if breathing is stopped and immediately call a doctor.
Due to its high level of toxicity, CO is a matter of concern also for control of Occupational Exposure Limits (OEL).

Due to its flammability CO shall be kept away from heat, hot surfaces, sparks, open flames, and other ignition sources. ATEX regulations also apply to CO.
In case of leaking gas fire, it is recommended not to extinguish, and preferably stop the leak safely by isolating the source of leaking gas, this is because a CO fire is difficult to extinguish, also by extinguishing a CO fire it may allow a flammable gas cloud to build up.

Strong precaution and risk assessment must be performed in order to avoid any leaks in both Production and Customer installations and in case it is possible all precautions to monitor CO presence must be put in place.

7.4.3 Oxogas (Syngas)

Oxogas is mainly a mixture of Hydrogen and CO, so product safety and precaution must be referred to the most dangerous of the two, that is CO for toxicity and H_2 for flammability.

7.4.4 Liquid Hydrogen

In addition to the fire, explosion, and asphyxiation hazards for gaseous H_2, the main hazard associated with LHy is exposure to extremely low temperatures. Cold burns may occur from short contact with frosted lines and equipment. Because of its extremely cold temperature, all LHy equipment shall be designed for low temperature operation. On inadequately insulated equipment, air will condense and can lead to oxygen enrichment, as O_2 will preferentially condense before N_2. O_2 enriched air will increase the combustion rate of H_2 and other flammable substances. It is recommended that LHy transfer lines be vacuum insulated to minimise the formation of liquid air. Any LHy spills will rapidly vaporise and create an immediately flammable atmosphere, in the event of spillage evacuate the area. In the event of a fire, do not direct water spray at a LHy vent as water will freeze and can cause overpressure of equipment. Ground surfaces below LHy storage systems shall be constructed of non-combustible materials.

Reference is made to:
EIGA DOC 230: Safe Catalyst Handling in HyCO plants [29]

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Unless otherwise specified, the latest edition shall apply.

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