



SAFETY OF HYDROGEN, HYCO PRODUCTION AND CARBON CAPTURE

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Prepared by WG-14 Hydrogen Production

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Table of Contents

1	Introduction	1
1.1	Scope.....	1
1.2	Purpose	1
2	Definitions	1
2.1	Publication terminology	1
2.2	Technical definitions	2
3	Physical characteristics.....	2
4	General safety concerns	2
5	Safety Considerations Relating to HyCO Plant Design	5
5.1	Design safety process	5
5.2	HyCO specific engineering and design guidelines	7
6	Operational Safety and Maintenance	15
6.1	Normal operations	15
6.2	Work Permit Systems	15
6.3	ATEX zoning and compatibility of equipment	16
6.4	Management of Change (See also EIGA DOC 51 Management of Change).....	16
6.5	Isolation and Lockout/Tagout of systems for safe working	17
6.6	Purging and Inerting	18
6.7	Leak prevention	19
7	Quality & Product Safety	19
7.1	Typical purities for Hydrogen product.....	19
7.2	Typical contaminants in Hydrogen vs. production methods	20
7.3	Quality control in HyCO production	21
7.4	Product Safety	21
8	References.....	22
9	Additional references	24

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 (H₂), carbon monoxide (CO) and syngas (H₂ & CO) production facilities including carbon (CO₂) 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 H₂, CO and syngas production installations and equipment. This publication also covers H₂ production using electrolyzers, ammonia (NH₃) 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 H₂ 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
- CO₂ compression, liquefaction, or sequestration after CO₂ 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 H₂, 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 (CO₂) 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 kNm³/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 H₂ into O₂ 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, O₂ 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