Review of emerging techniques for hydrogen production from methane and refinery fuel gas with carbon capture

Date: January 2023

Contents

1. Introduction 5

2. Abbreviations / definitions 8

3. Study approach and activities 9

3.1. Overview of study approach 9

3.2. Long list of technologies 20

3.3. Technology screening 32

3.4. Short list of technologies 32

4. Technology overview 34

4.1. Feed gas pre-treatment 38

4.2. Feed gas pre-reforming 38

4.3. Hydrogen production 39

4.4. Air separation unit 46

4.5. CO shift 46

4.6. CO_2 capture 47

4.7. Hydrogen purification 52

4.8. Heat and condensate recovery 52

4.9. Power 53

5. Environmental considerations and guidance 54

5.1. Feed gas supply 54

5.2. Feed gas desulphurisation and pre-reforming 55

5.3. Reforming and CO shift 56

5.4. Process CO_2 capture from hydrogen product...57

5.5. CO_2 capture strategies specific to steam methane reforming 58

5.6. Post-combustion CO_2 capture from SMR furnace flue gas 59

5.7. CO_2 capture rate 62

5.8. Hydrogen product purification 63

5.9. Off-gas production from hydrogen purification 64

5.10. Heat integration and process cooling 65

5.11. Combustion 66

5.12. Oxygen production 67

5.13. Water treatment for re-use 69

5.14. Reliability and availability 70

5.15. Flexible operation 71

5.16. Monitoring and measurement 72

5.17. Flaring 74

5.18. Venting and purging 75

5.19. Unplanned emissions to the environment 76

5.20. Noise 76

6. Process performance parameters 78

6.1. Process / energy efficiency 80

6.2. Emissions 82

6.3. Carbon capture performance 84

7. Summary of stakeholder input 86

8. References 86

Appendices 89

Appendix A – Stakeholder engagement questionnaire 89

1. Introduction

During 2019 and 2020, the UK environmental regulators[1] ('the regulators') received pre-application enquiries from several operators who were proposing to build new or modified plants for the large scale production of hydrogen (H_2), using methane (CH_4) from natural gas and/or refinery fuel gas (RFG) as a feedstock, with associated carbon dioxide capture and storage (CCS).

It is anticipated that these H_2/CCS plants will be an important component of the UK Government climate change policy to achieve Net Zero carbon emissions by 2050. The UK Department for Business, Energy, and Industrial Strategy (BEIS) is promoting the development of hydrogen as a fuel and carbon capture usage and storage (CCUS) at several locations in the UK.

- UK hydrogen strategy - GOV.UK (www.gov.uk)
- UK carbon capture, usage and storage - GOV.UK (www.gov.uk)

[Note: The need to review techniques and develop further guidance notes covering hydrogen production by other routes / technologies as they arise, is recognised by the regulators.]

Large scale industrial production of hydrogen is a long-established process in the UK. The best available techniques (BAT) reference document (BRef) for the manufacture of hydrogen in oil refineries was published in 2015[2] and the BRef for the manufacture of hydrogen in ammonia plants was published in 2007[3]. Neither of these BRef documents considers hydrogen production when combined with CCS.

Where there is no relevant BRef, or where related BAT conclusions do not address all the potential environmental effects, the regulator must set permit conditions, including emission limit values, on the basis of best available techniques that it has determined for the activities or processes. This shall be after prior consultations with the operator following the

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[1] The Environmental Regulators for H_2/CCS are the Environment Agency (EA) in England, the Scottish Environment Protection Agency (SEPA) in Scotland, Natural Resources Wales (NRW) in Wales and the Northern Ireland Environment Agency (NIEA), an executive agency of the Department of Environment, Agriculture and Rural Affairs, in Northern Ireland.

[2] Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas, IED 2010/75/EU, 2015.

[3] Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers, 2007.

requirements in Article 14(6) of the Industrial Emissions Directive 2010/75/EU (IED) and give special consideration to the criteria for determining BAT in Annex III of the IED.

These criteria include, amongst others, review of comparable processes, types and quantity of emissions, energy efficiency, efficient use of raw materials and prevention or reduction of overall impact of emissions on the environment.

The UK regulators commissioned this emerging techniques review and produced a summary of emerging techniques guidance because there is no existing guidance that is specific to the production of hydrogen when combined with CCS. This is new technology and there is limited evidence or data available for performance of comparable sites.

This review details the key environmental issues to address and information about best practice available on a selection of hydrogen production with carbon dioxide capture options. After consultation with industry, the regulators consider these are the most likely to be proposed by applicants in the short to medium term (1 to 5 years).

The guidance is based on current information which is publicly available and also on information which has been provided at our request by industry.

The guidance is not a regulatory requirement. It does not have the same regulatory status as BAT reference documents or related BAT conclusions. However operators would need to explain and justify where alternatives to methods and performance described in the guidance are proposed. Operators are encouraged to make contact with the appropriate regulator at the earliest possible opportunity.

Where emission limit values (ELVs) are required to meet IED Chapter III Special Provisions for Combustion Plant or the Medium Combustion Plant Directive 2015/2193/EU (MCPD), these will be set in permits. Where an emission level associated with the best available technique (BAT-AEL) applies from a relevant BRef, these may also be set though the latter may be granted derogation for up to 9 months if the technology is considered emerging, to allow testing and use (IED Article 15(5)). Permit conditions will be set to protect the environment by ensuring environmental quality standards are met (Article 18).

The UK regulators envisage that the emerging techniques review and emerging techniques guidance will be used by:

- operators when designing their plants and preparing their application for an environmental permit
- their own staff when determining environmental permits

- any other organisation or members of the public who want to understand how the environmental regulations and standards are being applied

The scope of this review and guidance is limited to preventing or reducing emissions into the environment and does not cover other aspects such as safety.

The guidance document provides a framework for applications and permits and is based on information available at this time. Further information about the performance of the processes will become available as they are further developed and commence operation. The UK regulators will keep BAT and emerging techniques under review as required by Article 19 of IED.

The UK regulators would like to thank everyone who has provided data and helped in the production of this review.

2. Abbreviations / definitions

Abbreviation	Description
ASU	Air Separation Unit
ATR	Autothermal Reformer
BAT	Best Available Techniques
BEIS	Business, Energy, and Industrial Strategy
BRef	BAT Reference Document
CCR	Carbon Capture Readiness
CCS	Carbon Capture and Storage
CCUS	Carbon Capture Utilisation and Storage
DAA	Directly Associated Activity
EAL	Environmental Assessment Level
EIGA	European Industrial Gases Association
ELV	Emissions Limit Value
GHR	Gas Heated Reformer
GTL	Gas To Liquids (typically conversion of natural gas to liquid fuels)
HT	High Temperature
IEA	International Energy Agency
IED	Industrial Emissions Directive
LT	Low Temperature
MT	Medium Temperature
OTNOC	Other Than Normal Operating Conditions
POX	Partial Oxidation
PSA	Pressure Swing Adsorption
RFG	Refinery Fuel Gas
SEPA	Scottish Environment Protection Agency
SCR	Selective Catalytic Reduction
Shift	CO shift, also termed water gas shift, the reaction of carbon monoxide with water to produce hydrogen and CO_2
SNCR	Selective Non-Catalytic Reduction
SMR	Steam Methane Reformer
Syngas	Synthesis gas – a gas mixture containing carbon monoxide and hydrogen, with other components such as CO_2 and water also potentially present
TSA	Temperature Swing Adsorption
UK	United Kingdom
VSA	Vacuum Swing Adsorption

3. Study approach and activities

3.1. Overview of study approach

3.1.1. Definition of scope boundaries

This guidance considers production of hydrogen from methane[4] with CO_2 capture. The various process units in the scope boundary and interfaces are shown in Figure 1.

This guidance specifically excludes the following activities:

- upstream gas production, processing, compression
- hydrogen transportation
- CO_2 transportation and storage
- CO_2 emissions other than those directly related to the hydrogen production activity, such as in production of gas feedstock, in generation of imported electrical power, or in transportation and end use of hydrogen product

The above activities may form part of an integrated stationary technical unit for the purposes of an environmental permit, as directly associated activities (DAAs) or as regulated activities in their own right. In this case, it is expected that the best available techniques (BAT) against all these regulated activities and/or DAAs are identified in accordance with relevant BAT reference documents or guidance documents as appropriate.

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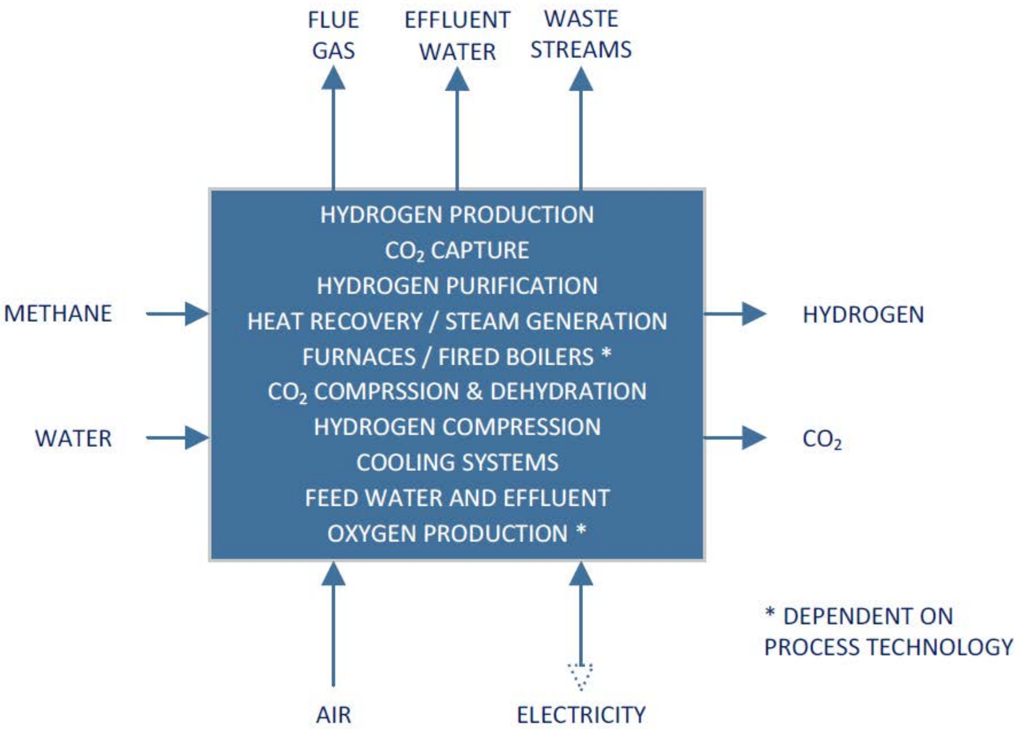
[4] Methane sources include natural gas from production / processing facilities, LNG import facilities, gas transmission or distribution networks; or refinery fuel gas derived from a range of off-gas streams within a refinery complex. Alternative sources of methane include biomethane or biosynthetic natural gas (BioSNG).

Figure 1 – Project scope boundaries



3.1.2. Scope boundaries – plant scale

This description of available techniques is intended to cover hydrogen production applications at a scale of hundreds of tonnes of hydrogen per day, designed for capture of the resultant CO_2 for storage.

Small scale production will be considered in future guidance, if descriptions and guidance in this document are deemed not to be applicable.

Several ongoing UK projects have proposed production capacity of 200 to 300 MW or greater of hydrogen energy[5] (based on lower heating value), equivalent to 144 to 216 t/day of hydrogen.

This does not represent a limit on individual hydrogen production train size, with 700 to 1500 MW output potentially feasible with some multiple equipment items in parallel, depending on production technology.

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[5] Hydrogen production of 300 MW lower heating value is equivalent to 100 kNm^3/h or 9,000 kg/h, with approximately 0.7 million tonnes per annum CO_2 capture.

3.1.3. Scope boundaries – feed and products

Feed and products boundaries, basis and exclusions are summarised in Table 1.

Table 1: Study boundaries – feed and products

	Description	Exclusions	Notes / Basis
Methane	Supply of methane rich feed gas, either natural gas or refinery fuel gas. Assumed to meet gas network quality, for example, Gas Safety (Management) Regulations, or local refinery fuel gas quality.	Excluding upstream gas production, processing, and transport.	Suitable pressure to feed hydrogen production process, for example from high pressure gas network. Feed gas compression may be required depending on the available source pressure. Additional process steps may be required, dependent on composition, for either natural gas or RFG feed gases. RFG streams in particular could contain various sulphur species including H_2S and organic sulphur compounds and impurities such as mercury, chlorides, and olefins.
Hydrogen	Hydrogen product quality suitable for combustion as an industrial or domestic fuel [Ref. 11].	Excluding production of hydrogen to 'fuel cell quality'.	For example, typical proposed specification [Ref. 11]: H2 ≥ 98 vol% * CO ≤ 20 ppmv CO2 + HCs ≤ 2 vol% * This is typical, and lower H_2 purity specifications may be practical, to make allowance for inerts such as nitrogen and argon from the feed gas and oxygen supplies passing with the hydrogen product,

			depending on the technology used for hydrogen purification. Pressure as delivered from production and purification process. Compression may be required for transportation / delivery to users.
Carbon dioxide	CO_2 meeting specification for downstream transportation (pipeline or shipping) and storage. Including CO_2 compression, dehydration and any purification requirements (for example, oxygen removal) depending on capture location, technology and impurities.	Excluding transportation and storage infrastructure, pipeline CO_2 compression or pumping, CO_2 liquefaction, and so on.	To pipeline quality specifications, considering oxygen, CO, H_2 and water content CO_2 quality requirements may vary depending on the transportation and storage infrastructure [Ref. 13]. There may be differences in CO_2 delivery pressure from the capture processes employed, impacting CO_2 compression requirements. CO_2 compression delivery pressure will depend on whether the CO_2 is to be transported in the gaseous or dense phase.

3.1.4. Scope boundaries – utilities

Utilities requirements for the hydrogen production and CO_2 capture processes are identified in Table 2.

Table 2: Study boundaries – utilities

	Description	Exclusions	Notes / Basis
Electrical power	Connection to network for import / export of electricity.		Dedicated power generation / heat to be included in boundary of assessment.

	Description	Exclusions	Notes / Basis
			A cogeneration plant may be considered where both steam production and power generation can be achieved, integrating steam and power systems in the hydrogen production and CO_2 capture processes, and where excess is produced to export to external users.
Water supply	Feed water for boiler / process, cooling water make up.	Excluding treatment, for example to towns water equivalent standard.	Production of demineralised boiler feed water and removal of impurities.
Air	Air for combustion or oxygen production (where required by process).		Including air compression and associated cooling for ASU.
Cooling	Process cooling requirements.		Cooling against air, closed or evaporative cooling water systems.
Fuel	Fuel for fired equipment – furnaces / heaters / boilers.		Produced within process (off gas or product hydrogen) or taken from feed gas.
Steam	At pressure levels to suit process requirements and heat integration.		Generated within plant boundary in heat exchange with process streams or from fired boiler / flue gas heat recovery systems. This is an area of potential integration with other industrial facilities for import or export of steam.

	Description	Exclusions	Notes / Basis
Flare	For combustion of non-routine controlled or emergency releases.		An elevated or ground flare system will be required to handle any controlled releases from planned and unplanned operations, such as start-up operation, planned or unplanned shutdown operation. Plant design should ensure that operations including planned start-up and shutdown minimise flaring, to limit emissions to air. Methods for monitoring / calculating flared gas volumes should be identified to confirm compliance with permit conditions.

3.1.5. Scope boundaries – emissions, effluents and wastes

Boundaries in terms of emissions, effluents and wastes are identified in Table 3.

Table 3: Study boundaries – emissions, effluents, and wastes

	Description	Exclusions	Notes / Basis
Emissions	Atmospheric emissions from combustion or other processes		Emissions considering any combustion activities, accounting for use of hydrogen rich fuels and impacts of post-combustion CO_2 capture where appropriate. Any continuous or intermittent venting or flaring – for example on start up. Loss of containment emissions.
Effluents	Liquid effluents		Effluent from cooling systems and steam systems.

	Description	Exclusions	Notes / Basis
			Water condensed in process, following water recovery. Aqueous effluents generated from emission abatement processes and solvent recovery / management activities.
Wastes	Any solid or liquid waste streams from operation	Excluding waste water, included under effluents above.	Degraded solvents, spent catalysts and adsorbents, considering recovery and recycling. Solids from process.

3.1.6. Key considerations for emerging techniques

Assessment of BAT criteria and emerging techniques should consider the following aspects where appropriate in technology selection, overall plant design, and development of operational philosophies and procedures.

Technology selection should include the following key environmental considerations:

- emissions to air
- emissions to water
- waste minimisation and waste treatment (liquid and solid waste streams)
- abatement techniques to reduce emissions (for example, airborne species resultant from solvent degradation)
- CO_2 capture rate
- energy efficiency
- hydrogen losses
- treatment of captured CO_2 for transport (for example, quality requirements)

Plant design and operations should address the considerations above and also those following, with reference to existing relevant standards where appropriate:

- monitoring standards for stack emissions (including averaging periods for dispersion modelling)
- monitoring standards for discharges to water (including averaging periods and arrangements for flow monitoring)
- air dispersion modelling standards
- ambient / deposition monitoring standards
- noise (for example, in compression of captured CO_2, fans, burners)
- maximising energy efficiency (including heat integration and optimisation, considering for example opportunities for heat recovery from compression systems)
- water use efficiency (for process use and cooling systems)
- optimisation of use of raw materials
- start-up and shutdown of operations (including ramp rates)
- other than normal operating conditions
- accident management, leak monitoring and containment arrangements, including loss of containment emissions
- monitoring for emissions of CO_2

3.1.7. Existing BAT reference documentation

Existing BAT reference (BRef) documents, relevant to the technologies covered in this report, are identified in Table 4. The Industrial Emission Directive 2010/75/EU Article 14 (6) and Annex III must be consulted to ensure compliance with the stated requirements.

Table 4: List of existing BAT reference documentation

Existing BAT reference	Subject (as relevant to this review)
Reference document on best available techniques for manufacture of large volume inorganic chemicals – Ammonia, Acids and Fertilisers, 2007	Steam reforming, autothermal reforming, hydrogen purification
Best available techniques (BAT) reference document for the refining of mineral oil and gas, IED 2010/75/EU, 2015, EUR 27140 EN BAT conclusions for the refining of mineral oil and gas (2014/738/EU)	Hydrogen production (partial oxidation, steam reforming, gas heated reforming and hydrogen purification) Energy efficiency techniques (heat integration / recovery and steam management)

Existing BAT reference	**Subject (as relevant to this review)**
Best available techniques (BAT) reference document for common waste water and waste gas treatment / management systems in the chemical sector, IED 2010/75/EU, 2016, EUR 28112 EN BAT conclusions for common waste water and waste gas treatment / management systems in the chemical sector (2016/902/EU)	Waste water collection and treatment process integrated measures
Best available techniques (BAT) reference document for large combustion plants, IED 2010/75/EU, 2017, EUR 28836 EN BAT conclusions for large combustion plants (2017/1442/EU)[6, 7]	Best available techniques for large combustion plants, including measures to reduce emissions of pollutants from combustion processes and BAT-associated emission levels and energy efficiency levels for large combustion plants.
Reference document on the application of best available techniques to industrial cooling systems, 2001	Cooling water systems
Reference document on best available techniques for energy efficiency, 2009	Energy efficiency and integration management
Reference document on the general principles of monitoring, (2003)	Monitoring of emissions to air and water

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[6] The Industrial Emission Directive 2010/75/EU Chapter III and Annex V set the minimum requirements for certain pollutant emissions from LCPs.

[7] Directive (EU) 2015/2193 on the limitation of emissions of certain pollutants into the air from MCPs known as the Medium Combustion Plant Directive (MCPD) regulates pollutant emissions from the combustion of fuels in plants with a rated thermal input equal to or greater than 1 MWth and less than 50 MWth.

3.1.8. Other relevant guidance documentation

Guidance documents, potentially relevant to the technologies covered under this report, are included in Table 5.

Table 5: List of guidance documentation – UK environmental regulators

Existing guidance and documentation	Subject (as relevant to this review)
Carbon capture readiness (CCR) A guidance note for section 36 Electricity Act 1989 consent applications, URM 09D/810 November 2009 and amendments.	Process CO_2 capture Post-combustion CO_2 capture
UK TWG 18 submission for combustion sector BRef note revision, carbon capture technology and carbon capture ready criteria, 31/5/2012	Process CO_2 capture Post-combustion CO_2 capture
Review of amine emissions from carbon capture systems, SEPA, 2015	Post-combustion CO_2 capture amine scrubbing systems
Water demand for carbon capture and storage (CCS), Environment Agency November 2012	Process CO_2 capture Post-combustion CO_2 capture
BAT review for new-build and retrofit post-combustion carbon dioxide capture using amine-based technologies for power and CHP plants fuelled by gas and biomass as an emerging technology under the IED for the UK. Post-combustion carbon dioxide capture: best available techniques (BAT) **[Ref. 6, 21]**	Post-combustion CO_2 capture

Existing guidance and documentation	Subject (as relevant to this review)
BAT for new build oxyfuel carbon capture coal-fired plants, V1.9 – May 2015 [Ref. 12]	ASUs
Reference document on the general principles of monitoring, (2003)	Monitoring of emissions to air and water

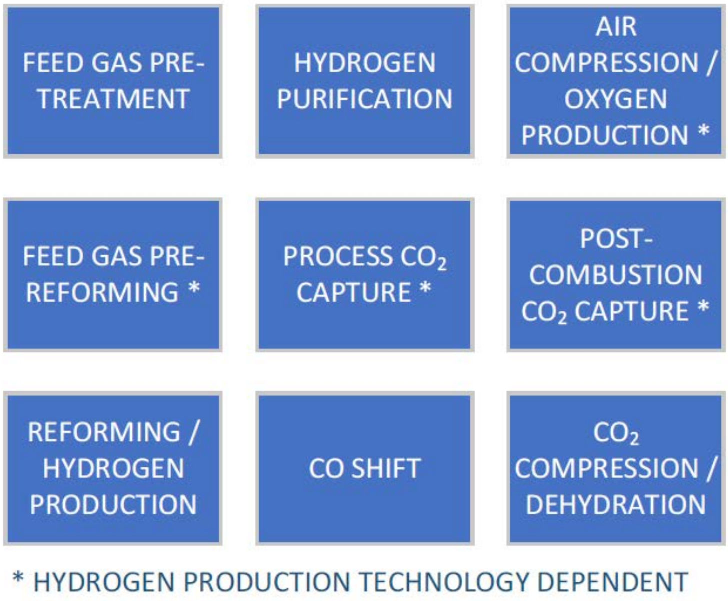
List of guidance documentation – industry

- EIGA, IGC Document 155/21 [Ref. 17]. Best available techniques for hydrogen production by steam methane reforming
- EIGA, IGC Document 88/14 [Ref. 18]. Good environmental management practices for the industrial gas industry
- EIGA, Document 122/18 [Ref. 16]. Environmental impacts of hydrogen plants

3.2. Long list of technologies

The main process steps for hydrogen production from methane with CO_2 capture are shown in Figure 2.

Figure 2 - Main process steps for hydrogen production from methane with CO_2 capture



Available technologies, including established technologies and emerging technologies, are first identified through literature review of technical reports available in the public domain. This includes publications from international organisations, UK organisations, UK academies, professional institutions, and European industry trade associations.

The readiness of the technology for commercial deployment is categorised as follow:

- ‘Mature’ is defined as a technology proven at large scale in manufacturing for the stated industries. Scale up of some elements may still be required.
- ‘Novel at Scale’ is defined as a technology proven at a smaller scale or in other industries – for example, for chemical production.
- ‘Low’ is defined as a technology being studied at Research and Development level and not yet proven at a pilot scale for manufacturing in the stated industries.

3.2.1. Feed gas pre-treatment

Feed gas pre-treatment consists of the removal of contaminants to prevent any catalyst poisoning in the downstream processes - mainly sulphur species and mercury species. Refinery fuel gas can also contain chlorides and heavy metals requiring removal.

Feed gas pre-treatment requirements are dependent on the hydrogen production technology, with some steps being optional. For example, with non-catalytic partial oxidation (POX) technology, depending on feed gas impurity levels, treatment may be needed only to protect the CO shift catalyst downstream of the POX reactor.

Available pre-treatment technologies for sulphur removal are mature and include:

- catalytic reaction to hydrogenate any organic sulphur or organic chlorides to H_2S and HCl respectively
- absorption in a metal oxide bed to form metal sulphide or metal chloride

Where the sulphur content is higher, for example in refinery fuel gas streams, other sulphur removal technologies may be more practical and economical.

Available pre-treatment technologies for mercury removal are also well-established and include, for example, absorption on a metal sulphide bed.

Feed gas pre-treatment is further described in section 4.1.

3.2.2. Feed gas pre-reforming

Feed gas pre-reforming converts the feed gas heavier hydrocarbons into methane. Conversion of the heavier hydrocarbons reduces potential to form carbon in the reformer, and also forms some hydrogen and CO_2.

Feed gas pre-reforming technology is mature and consists of a catalytic reaction using nickel-based catalyst. Feed gas pre-reforming is further described in section 4.2.

For hydrogen production using the non-catalytic POX technology, feed gas pre-reforming is not necessary.

3.2.3. Oxygen production

Oxygen is required for hydrogen production using autothermal reforming (ATR)[8] and partial oxidation (POX) technologies. Technologies for oxygen production include cryogenic and non-cryogenic air separation.

Table 6: Technology long list – oxygen production

Oxygen production technology	Readiness level	Most quoted technologies
Cryogenic air separation	Mature	Cryogenic package including TSA and fractionation
Non-cryogenic air separation	Mature	PSA, VSA, Membrane
Non-cryogenic air separation	Low	Ceramic membranes

Cryogenic air separation

Cryogenic air separation is a mature technology that can produce a high volume of oxygen at high purity (>99.5% O_2). The air separation unit (ASU) will include air compression to multiple pressure levels; air drying and purification using temperature swing adsorption; highly integrated multi-stream heat exchange and cryogenic fractionation in a cold box module; expansion of gases in cryogenic turbo expanders; and cryogenic pumping of oxygen [Ref. 19].

Using cryogenic air separation, liquid oxygen can be produced and stored as a back-up supply.

Very large scale high purity / high pressure oxygen production is conventional for example in gas to liquids production. The Pearl GTL plant at Ras Laffan, Qatar, which uses gas POX

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[8] ATR can also be air-blown, producing a nitrogen / hydrogen syngas which could be used as a zero carbon fuel for example for existing gas turbines that would otherwise require steam as a diluent.

technology for production of hydrogen, includes 8 x 3,600 tonnes per day (tpd) oxygen plants. Capacities of over 5,000 tonnes per day of oxygen are possible.

Non-cryogenic air separation

Non-cryogenic air separation technologies are also mature, but used for lower volume oxygen production and/or lower purity (for example, between 85% and 95%), not meeting with the needs for large scale hydrogen production. The most common non-cryogenic air separation technologies are PSA, VSA and membrane technologies [Ref. 19]. Air separation by pressure swing adsorption (PSA), vacuum swing adsorption (VSA), or membrane separation is not currently appropriate at the required large scale and high oxygen purity.

Emerging technologies such as ceramic membranes for air separation are a potential future technology, not currently commercially available.

Other sources of oxygen

Oxygen as by-product of green hydrogen production (electrolysis of water) could potentially supplement supply and provide incremental improvement in overall efficiency where facilities can be co-located, although such schemes are immature, and it is not expected that this will be a route to large scale oxygen supply in the short term. The oxygen would be produced at low pressure and would require compression to deliver at the pressure required for hydrogen production.

3.2.4. Hydrogen production technologies

Technologies for hydrogen production from methane are listed in Table 7, including associated level of readiness for deployment for hydrogen production with CO_2 capture.

Table 7: Technology long list – hydrogen production

Hydrogen production technology	Readiness level	Industries used
Steam methane reforming (SMR) [Ref. 2] (+ Pre-reforming)	Mature	Methanol, Refining, Petrochemical
Autothermal reforming (ATR) [Ref. 2]	Mature	Ammonia Methanol, Gas To Liquids (GTL)
Combined SMR and ATR [Ref. 4]	Mature	Ammonia Methanol
Combined gas heated reforming (GHR) and SMR [Ref. 22]	Novel at Scale (Combination not demonstrated at large scale)	Ammonia Methanol
Partial oxidation [Ref. 2]	Mature	Ammonia, Methanol, Gas To Liquids (GTL)
Combined GHR and oxygen-blown ATR, parallel configuration [Ref. 4]	Mature	Hydrogen
Combined GHR and oxygen-blown ATR, Series [Ref. 4]	Mature	Ammonia Hydrogen Methanol

Hydrogen production technology	Readiness level	Industries used
Sorption enhanced steam methane reforming (SE-SMR) [Ref. 7][9]	Low	Hydrogen
Pyrolysis [Ref. 2]	Low	Hydrogen
Microwave technologies [Ref. 2]	Low	Hydrogen
Dry reforming	Low	Hydrogen
Plasma reforming	Low	Hydrogen
Solar SMR	Low	Hydrogen
Tri-reforming of methane	Low	Hydrogen

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[9] Bulk Hydrogen by Sorbent Enhanced Steam Reforming (HyPER), led by Cranfield University, is being supported under Phase 2 of the BEIS UK Hydrogen Supply Competition to demonstrate this novel technology at pilot scale, Hydrogen Supply Competition Phase 2 successful projects - GOV.UK (www.gov.uk)

3.2.5. CO shift technologies

CO shift is a catalytic reaction, which converts CO and water (steam) to hydrogen and CO_2. The CO shift process is further defined in section 4.3.

Technologies for CO shift (water gas shift) are listed below, including associated level of readiness for deployment for large scale hydrogen production with CO_2 capture.

Table 8: Technology long list – CO shift (water gas shift)

CO shift technology	Readiness level	Relevant industries
High temperature (HT) CO shift conversion HT operation at 300 to 450°C ~2.5% mol CO dry basis at reactor outlet	Mature	Ammonia Hydrogen
Medium temperature (MT) CO shift conversion MT operation at 220 to 270°C ~0.5% mol CO dry basis at reactor outlet	Mature	Hydrogen
High temperature / low temperature (HT/LT) CO shift conversion LT operation at 180 to 230°C ~0.2% mol CO dry basis at reactor outlet	Mature	Ammonia Hydrogen
Isothermal CO shift conversion Operation at MT or LT level for high conversion to CO, with heat exchange within the reactor to produce steam. An inlet temperature of 240°C is typical,	Mature	Ammonia Hydrogen

CO shift technology	Readiness level	Relevant industries
peaking at 280 to 300°C, with outlet pressure at an approach to the steam production temperature. ~0.5% mol CO dry basis at reactor outlet		
CO sour shift Used for syngas streams containing H_2S. The sour shift converts CO with water to H_2 and CO_2. The shifted gas contains acid gas (both H_2S and CO_2).	Mature	Ammonia Methanol Hydrogen
Sorption enhanced CO shift	Low	Hydrogen

3.2.6. CO_2 capture technologies

For low carbon hydrogen production from methane, CO_2 can potentially be captured as follows:

- process CO_2 capture – from process streams such as hydrogen product downstream of CO shift, with advantages of high pressure and/or high CO_2 concentration (upwards of 24 vol% depending on the hydrogen production technology)
- post-combustion CO_2 capture – from combustion flue gases such as from reformer furnace, at near atmospheric pressure, with relatively low CO_2 concentration (around 10 to 20 vol%) and in the presence of oxygen, nitrogen, and other combustion products

For process CO_2 capture both physical and chemical absorption are potentially applicable technologies. In post-combustion capture, chemical absorption is the only option due to the low partial pressure of CO_2.

Process CO_2 capture technologies and post-combustion CO_2 capture technologies are listed in Table 9, along with their associated level of readiness for deployment.

Table 9: Technology long list – process CO_2 capture

Process CO_2 capture technology	Readiness level [Ref. 10]	Most quoted technologies [Ref. 10]
Absorption – chemical solvents	Mature	Amine solvents, for example, formulated MDEA solvents, Amine Guard FS (UCARSOL®), aMDEA, ADIP ULTRA Hot potassium carbonate (for example, Benfield®, Catacarb®)

Process CO_2 capture technology	**Readiness level [Ref. 10]**	**Most quoted technologies [Ref. 10]**
Absorption – physical solvents	Mature	DEPG[10] (for example, Selexol® Genosorb®) Methanol (for example, Rectisol®) n-methyl-2-pyrrolidone (for example, Purisol®)
Absorption – hybrid solvents	Mature	for example, Sulfinol®[11]
Cryogenic separation	Novel at Scale	Low temperature partial condensation for bulk CO_2 separation, downstream of CO shift or on compressed PSA tail gas
Membrane separation	Low	H2 membrane integrated into ATR for example, MTR Polaris® for example, Carbon Molecular Sieve (CMS) membrane
Chemical looping reforming [Ref. 2]	Low	Metal oxide
Pressure swing adsorption (PSA)	Mature	Adsorber beds with pressure swing regeneration

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[10] Dimethyl ethers of polyethylene glycol

[11] Tetrahydrothiophene 1,1-dioxide (Sulfolane), an alkaloamine and water

Process CO_2 capture technology	Readiness level [Ref. 10]	Most quoted technologies [Ref. 10]
Vacuum swing adsorption (VSA)	Novel at Scale (Demonstrated at large scale, but limited references)	Adsorber beds with vacuum swing regeneration

Table 10: Technology long list – post-combustion CO_2 capture

Post-combustion CO_2 capture technology	Readiness level [Ref. 10]	Most quoted technologies [Ref. 10]
Absorption - chemical solvents	Novel at Scale (Demonstrated at large scale but limited references)	Amine solvents for example, MEA based processes such as Fluor Econamine FG Plus^{SM} or proprietary amine processes such as Shell CANSOLV® or MHI KS-1^{TM}, a hindered amine
Absorption - chemical solvents	Low	Ammonia Amino-acid Hot potassium carbonate Proprietary non-amine solvents
Membrane separation	Low	for example, MTR Polaris® Metal oxide
Chemical looping combustion	Low	Adsorber beds with regeneration

Post-combustion CO_2 capture technology	Readiness level [Ref. 10]	Most quoted technologies [Ref. 10]
Solid sorbents	Low	Zeolites, metal-organic frameworks, amine impregnated solids

3.2.7. Hydrogen purification technologies

Hydrogen purification technologies are listed with their associated level of readiness for deployment in Table 11.

Table 11: Technology long list – hydrogen purification

Hydrogen purification technology	Level of readiness	Most quoted technologies
Adsorption - PSA	Mature	Adsorber beds with pressure swing regeneration
Methanation	Mature	Nickel based catalysts

3.2.8. CO_2 dehydration

CO_2 streams are typically produced at low pressure, requiring compression and dehydration prior to delivery to CCS transportation and storage infrastructure. A large proportion of water will be condensed and separated as the CO_2 is cooled after each compression stage.

There are two main techniques for dehydration of CO_2, both mature and widely used:

- temperature swing adsorption, for example, using molecular sieve in a fixed bed, regenerated by passing hot CO_2 gas over the bed to desorb water. Cooling of the regeneration gas allows water to be condensed and separated
- glycol absorption, for example, with counter-current contact of CO_2 and circulating tri-ethylene glycol solvent. Thermal regeneration is used to strip water from the rich glycol solvent

It may also be necessary to remove oxygen from CO_2 from post-combustion capture, which can be achieved by catalytic reaction with hydrogen. As the temperature requirements are modest at around 80°C, the reactor can be located between the CO_2 compressor and aftercooler, prior to dehydration.

3.3. Technology screening

A high level screening of technologies has been conducted against the scope boundaries.

The short list of technologies is based on consideration of:

- technologies that can achieve the production scale that are likely to be proposed in line with UK decarbonisation objectives
- technologies with a suitable level of readiness for deployment:
    - mature technologies applied in equivalent service and at the required scale and design operating envelope (for example, pressure)
    - combinations of technologies proven in operation, but not previously combined in equivalent service or at the required scale

The short list of technologies excludes technologies with low readiness level.

- existing hydrogen production technologies that may be a candidate for retrofit of CO_2 capture
- technologies that are being considered for current UK projects

3.4. Short list of technologies

This short list of technologies that may be employed in hydrogen production with CO_2 capture, represents a current view of available technologies and may require update in the future as novel technologies come forward and are ready for deployment.

Technologies short list

Feed gas sulphur pre-treatment

- hydrogenation and H_2S removal with metal oxide

Feed gas mercury pre-treatment

- mercury removal unit with activated carbon
- mercury removal unit with metal sulphide

Pre-reforming (optional)

- pre-reformer with catalyst bed

Hydrogen production

- steam methane reforming (SMR)
- autothermal reforming (ATR)
- gas heated (convective) reforming (for example, GHR+ATR or GHR+SMR)
- partial oxidation (POX)

Oxygen production

- cryogenic air separation unit (ASU)

CO shift

- high temperature CO shift
- high temperature / low temperature CO shift
- isothermal CO shift
- sour CO shift

Process CO_2 capture

- chemical solvent absorption (for example, amine)
- physical solvent absorption
- hybrid solvent absorption
- low temperature separation
- vacuum swing adsorption (VSA)

CO_2 dehydration

- molecular sieve temperature swing adsorption (TSA)
- tri-ethylene glycol (TEG) Absorption

Post-combustion CO_2 capture

- chemical solvent absorption – amines

Hydrogen purification

- pressure swing adsorption (PSA)
- methanation

4. Technology overview

In this section, a technology overview is provided for the main processes involved in hydrogen production from methane with CO_2 capture under three different hydrogen production schemes:

- hydrogen production from methane using SMR technology with CO_2 capture (Fig.3) In the reforming section, the SMR can be combined with a gas heated reformer (GHR)
- hydrogen production from methane using ATR technology with CO_2 capture (Fig.4) In the reforming section, the ATR can be combined with a gas heated reformer (GHR)
- hydrogen production from methane using POX technology with CO_2 capture (Fig.5)

Each block flow diagram identifies:

- the main process steps for hydrogen production (in purple)
- the main process steps for CO_2 capture (in orange)
- the feed gas and associated products and by-products (in purple)
- the associated utility systems, power, heat recovery and steam generation (in blue)
- the waste recovery and recycling systems (in green)
- the scope of this guidance (within the dotted blue line)

Figure 3 – Block flow diagram of SMR technology with carbon capture

(Typical – Other configurations are possible, for example, with addition of gas heated reformer)

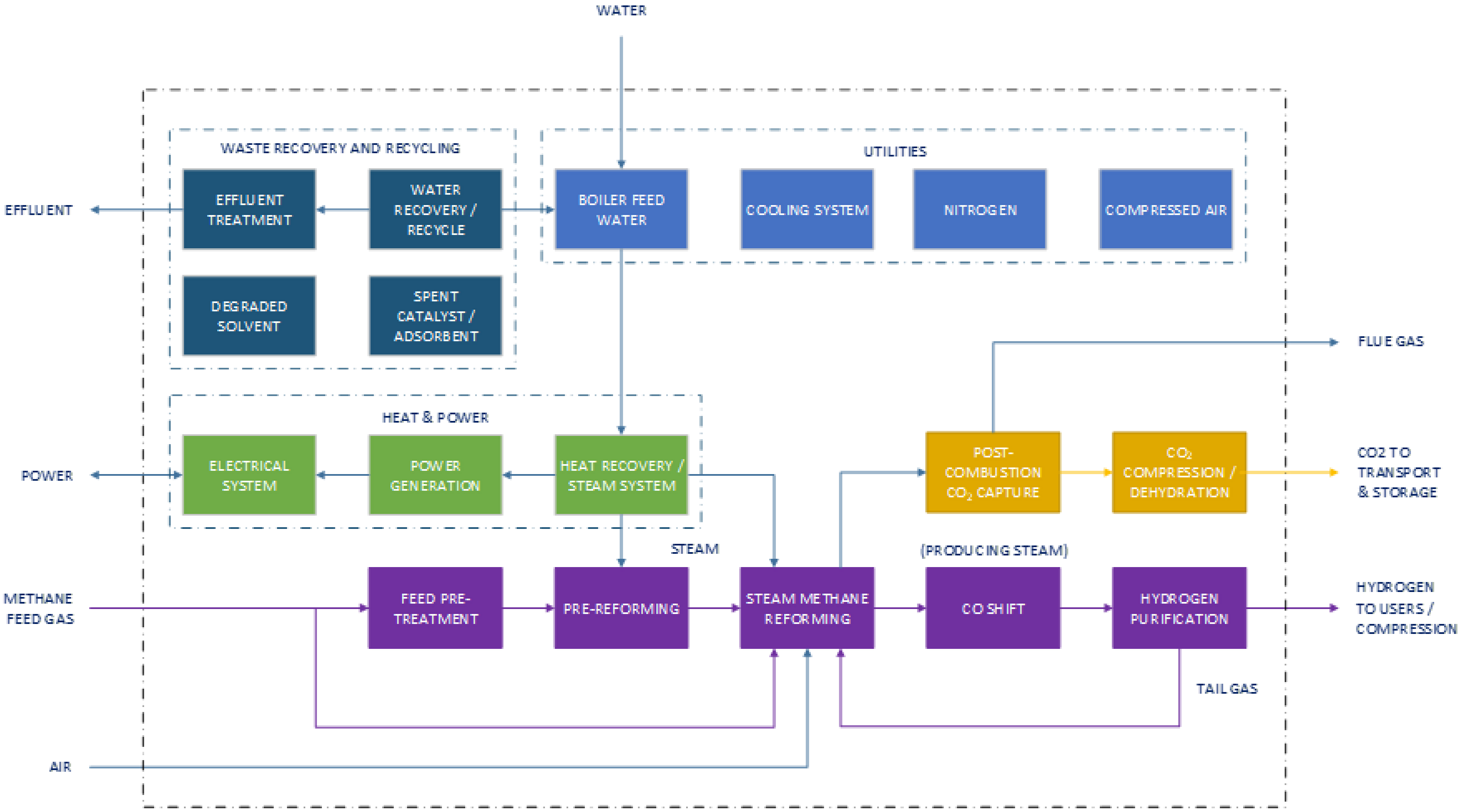


Figure 4 – Block flow diagram of ATR technology with carbon capture

(Typical – other configurations possible, for example, with addition of gas heated reformer)

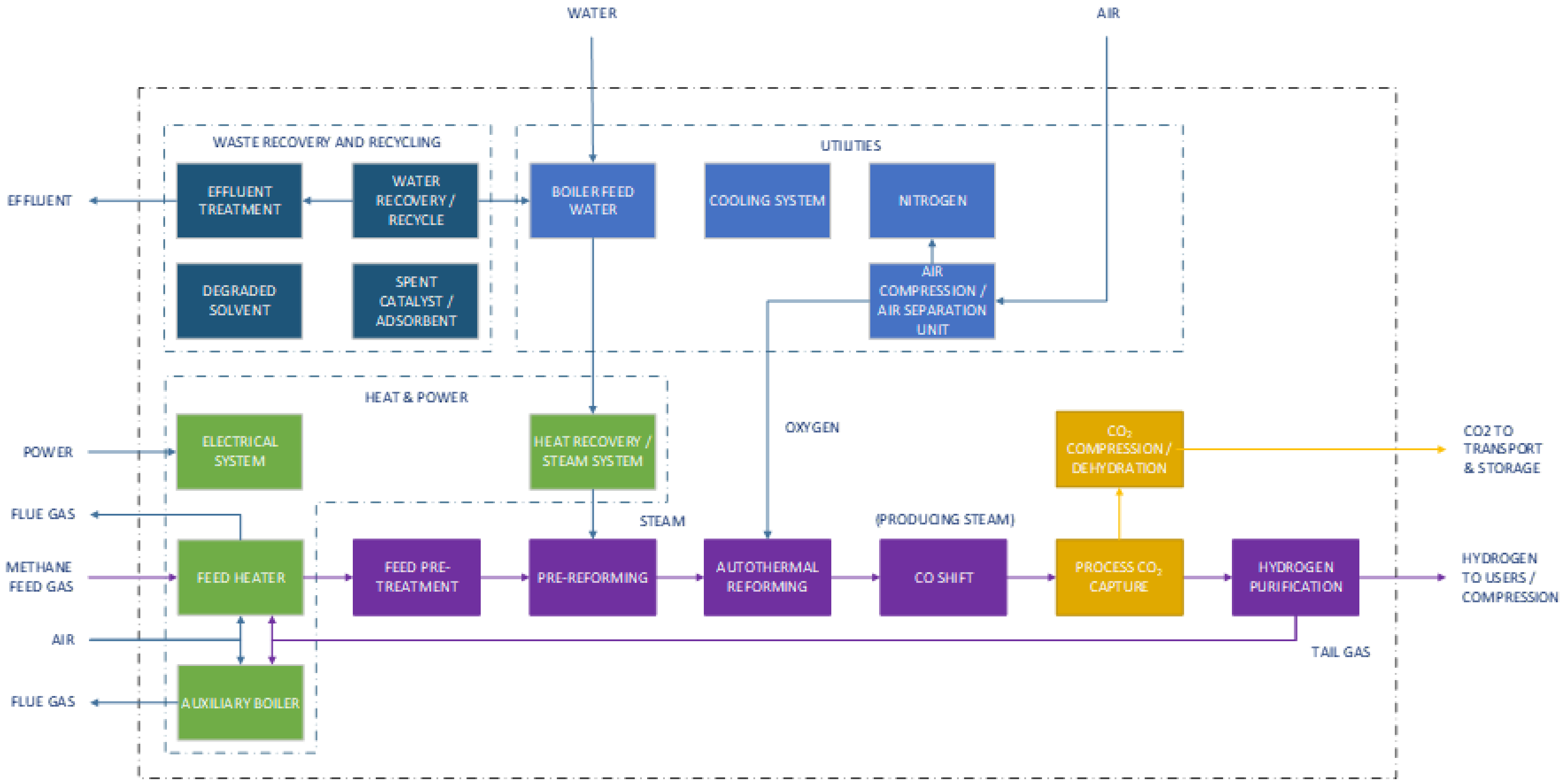
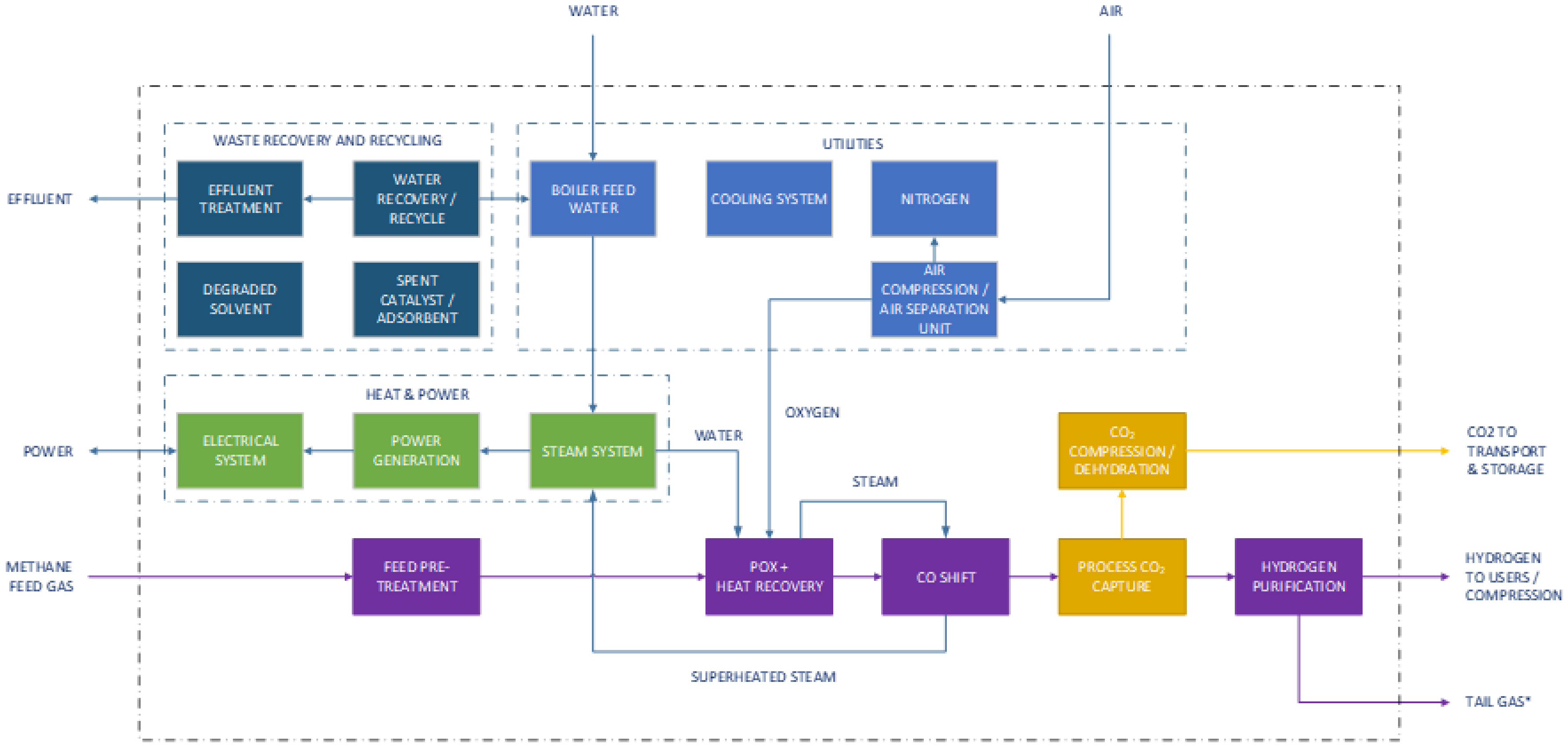


Figure 5 – Block flow diagram of POX technology with carbon capture

(Typical – Other configurations are possible)



* DEPENDENT ON HYDROGEN PURIFICATION TECHNOLOGY - METHANATION FOR EXAMPLE PRODUCES NO TAIL GAS.

4.1. Feed gas pre-treatment

4.1.1. Sulphur removal

The feed gas, natural gas or RFG, may require to be first pre-treated to remove any sulphur species to prevent poisoning and deactivation of the reforming and CO shift catalysts. Sulphur treatment includes hydrogenation using catalyst based technology such as cobalt molybdenum to convert the sulphur species to H_2S, which is then absorbed on a zinc oxide bed. The feed gas is preheated to 200 to 400°C. The chemical reactions occurring in the sulphur removal step are shown in Table 12.

Table 12: Sulphur removal chemical reactions

Chemical reactions	
Hydrogenation	$R\text{-}SH + H_2 \rightleftharpoons H_2S + RH$
Desulphurisation	$H_2S + ZnO \rightleftharpoons ZnS + H_2O$

4.1.2. Mercury removal

The feed gas, natural gas or RFG, may require to be first pre-treated to remove any mercury species to prevent poisoning and deactivation of the downstream reforming catalyst. Mercury removal step includes a mercury removal unit, which would typically consist of fixed bed reactor with an adsorbent. Elemental mercury removal is achieved either by reaction with sulphur-impregnated activated carbon (S) or with a metal sulphide (MeS) and forms a stable solid of mercury ore called cinnabar on the adsorbent. The chemical reactions occurring in the mercury removal step are shown in Table 13.

Table 13: Mercury removal chemical reactions

Chemical reactions	
Elemental sulphur reaction	$Hg^0 + S \rightleftharpoons HgS$
Metal sulphide reaction	$Hg^0 + 2MeS \rightleftharpoons HgS + Me_2S$

4.2. Feed gas pre-reforming

Pre-reforming is an optional step that can be required upstream of a SMR or ATR for processing feed streams containing heavier hydrocarbons such as ethane, propane and butane, and to increase robustness to varying feed gas composition The pre-reforming step converts the feed gas heavier hydrocarbons into methane in a steam reforming step using a nickel based catalyst and operating at lower temperature than that of the main reforming process (450 to 500°C).

By converting the heavier hydrocarbons into methane, the pre-reforming step reduces the required tube area, energy consumption and NO_x emissions in the case of SMR technology due to decreased firing in the main reformer. In the case of ATR technology, it reduces the oxygen and energy consumption.

The chemical reactions occurring in steam methane pre-reforming are shown in Table 14.

Table 14: Pre-reforming chemical reactions

Chemical reactions	
Pre-reforming (1)	$(CH_2)_n + nH_2O(g) \rightleftharpoons nCO + 2nH_2$
Pre-reforming (2)	$(CH_2)_n + 2nH_2O(g) \rightleftharpoons nCO + 3nH_2$
Water gas shift	$CO + H_2O(g) \rightleftharpoons H_2 + CO_2$

4.3. Hydrogen production

4.3.1. Steam methane reforming (SMR) and shift technology

In steam methane reforming, methane reacts with steam and is converted to hydrogen and carbon monoxide using a nickel catalyst. The carbon monoxide produced as part the methane / steam reaction then reacts with steam (through water gas shift reaction) increasing the hydrogen yield and producing CO_2. The chemical reactions occurring in steam methane reforming are shown in Table 15.

Table 15: Steam methane reforming and shift chemical reactions

Chemical reactions		
Steam methane reforming	$CH_4 + H_2O_{(g)} \rightleftharpoons CO + 3\ H_2$	ΔH_{298} = 206 kJ/mol
Water gas shift	$CO + H_2O_{(g)} \rightleftharpoons H_2 + CO_2$	ΔH_{298} = - 41 kJ/mol
Overall reaction *	$CH_4 + 2\ H_2O_{(g)} \rightleftharpoons CO_2 + 4\ H_2$	ΔH_{298} = 165 kJ/mol

* The reformer outlet will contain some unconverted methane and carbon monoxide. The water gas shift is an equilibrium reaction and 15 mol% carbon monoxide and 8% CO_2 would

be typical in the syngas at the outlet of the reforming process on a dry basis. This syngas is passed to water gas shift reactor(s), described in section 4.5, operating at optimal conditions to maximise hydrogen production and conversion of carbon monoxide to CO_2 for capture.

The incoming treated feed gas is preheated against the hot flue gas in the reformer convection section before entering the steam reformer tubes filled with nickel catalyst. As shown in Table 15, the reaction between methane and steam is endothermic hence heat is required to allow the reaction to take place. The steam reformer is heated via an external furnace with multiple burners combusting a fuel source with air.

The fuel source to the furnace burners typically consists of recycled tail gas from the downstream hydrogen purification process, supplemented with feed gas as a makeup fuel. Combustion heat from the reformer flue gas is recovered via a waste heat recovery process to generate steam and to preheat other process streams to maximise energy efficiency. The water gas shift process is exothermic allowing significant production of additional steam.

4.3.2. Autothermal reforming (ATR) and shift technology

In autothermal reforming (ATR), methane is first partially oxidised by oxygen to produce hydrogen and carbon monoxide. Contrary to the steam methane reformer, the autothermal reactor does not require any heat from an external furnace. The partial oxidation reaction is exothermic and provides the required heat to the steam reforming reaction in which methane and steam reacts to produce carbon monoxide and hydrogen in the reformer fixed catalyst bed. The chemical reaction occurring in autothermal reforming are shown in Table 16.

Table 16: Autothermal reforming and shift chemical reactions

Chemical reactions		
Methane partial oxidation	$CH_4 + O_2 \rightleftharpoons CO + 2\ H_2$	$\Delta H_{298} = -36$ kJ/mol
Steam methane reforming	$CH_4 + H_2O_{(g)} \rightleftharpoons CO + 3\ H_2$	$\Delta H_{298} = 206$ kJ/mol
Combined ATR reaction *	$CH_4 + O_2 + H_2O_{(g)} \rightleftharpoons CO + H_2$	$\Delta H_{298} = 85$ kJ/mol
Water gas shift	$CO + H_2O_{(g)} \rightleftharpoons H_2 + CO_2$	$\Delta H_{298} = -\ 41$ kJ/mol
Overall reaction	$CH_4 + O_2 + H_2O_{(g)} \rightleftharpoons CO_2 + H_2$	$\Delta H_{298} = 44$ kJ/mol

* Based on notional 50:50 split between the methane partial oxidation and steam methane reforming reactions. The reformer outlet will contain some unconverted methane, and the water gas shift reaction within the reformer will lead to a mixture of methane, hydrogen,

carbon monoxide, CO_2 and water in the syngas at the outlet. This syngas is passed to water gas shift reactor(s), described in section 4.5, operating at optimal conditions to maximise hydrogen production and conversion of carbon monoxide to CO_2 for capture.

Oxygen required for the partial oxidation reaction is separated from air, typically cryogenically.

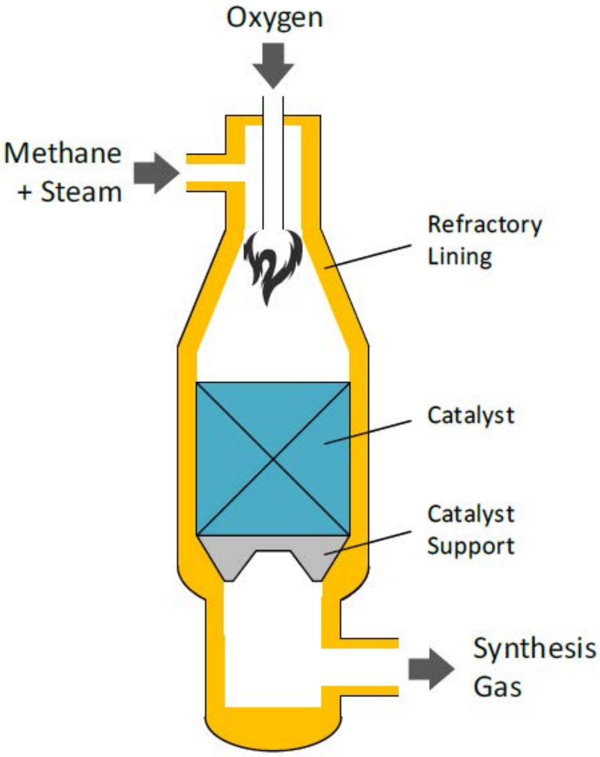
The partial oxidation reaction occurs in the top section of the autothermal reformer. The top section is fitted with a burner where methane and oxygen are mixed in a diffusion flame.

The steam methane reforming reaction occurs in the catalytic bed area, which is located in the bottom section of the reformer. The arrangement of a typical autothermal reformer is shown in Figure 6.

The risk of soot formation exists due to the partial oxidation (reducing atmosphere) and may depend on the following parameters: feed composition, temperature, pressure, burner design, and flow conditions in the combustion zone [Ref. 3]. The catalyst bed immediately downstream may be selected such that any identified soot precursors are destroyed going through the catalytic bed to avoid soot deposition on the catalyst surface, which would reduce heat transfer.

The main differences compared with the steam reforming (SMR) process are the addition of an ASU and feed pre-heater furnace, the absence of an external reformer furnace and associated convective section. There are benefits such as the ability to capture CO_2 from the process without post-combustion capture, and also more rapid production ramping for flexible operation.

Figure 6 – Typical autothermal reformer



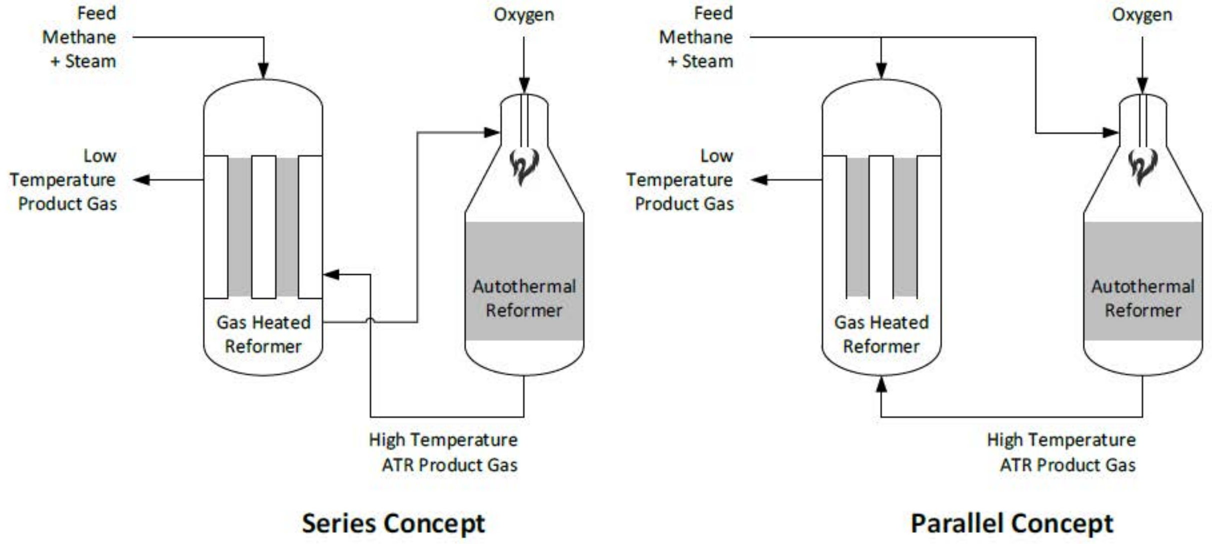
4.3.3. Convective reforming technology

Gas heated reforming (GHR) is an alternative approach to conventional steam reforming. A gas heated reformer consists of a vertical vessel containing tubes filled with catalyst and has a more compact footprint than a steam methane reformer due to the heat transfer being convective rather than radiative.

A gas heated reformer can be used in combination with an autothermal reformer or a steam methane reformer to increase conversion, although it is most commonly seen in combination with an autothermal reformer. A gas heated reformer does not require any external furnace, as the hot main reformer exit gas provides the heat required for the additional endothermic reforming reaction to take place within the gas heated reformer.

GHR and ATR can be used in a series concept or parallel concept, as shown in Figure 7. Similar schemes combining GHR with SMR are possible.

Figure 7 – Convective reforming concepts



In the series concept, the methane and steam feed streams are fed to the GHR where part of the methane is reformed. Partially converted syngas stream from the GHR is then transferred to the ATR for further syngas conversion. The hot syngas produced in the ATR is fed back to the GHR to provide the heat required for the endothermic steam methane reforming reaction to take place via counter current heat exchange. The cooled syngas leaves the GHR and passes to the downstream water-gas shift unit.

In the parallel concept, the methane and steam feed streams are fed to both the GHR and the ATR. The hot gas from the ATR is mixed with the cooler gas leaving the GHR tubes. This mixed gas flows up the shell side of the GHR is cooler and the gas temperature exiting the tube side of the GHR is cooler than in the series scheme.

On a like for like basis, the series concept will minimise methane slip and maximise overall CO_2 capture rates. Additional steam feed would be required to the GHR to compensate for the lower reforming temperature (compared to the ATR outlet temperature) and reduce methane slip from the GHR.

4.3.4. Partial oxidation (POX) technology

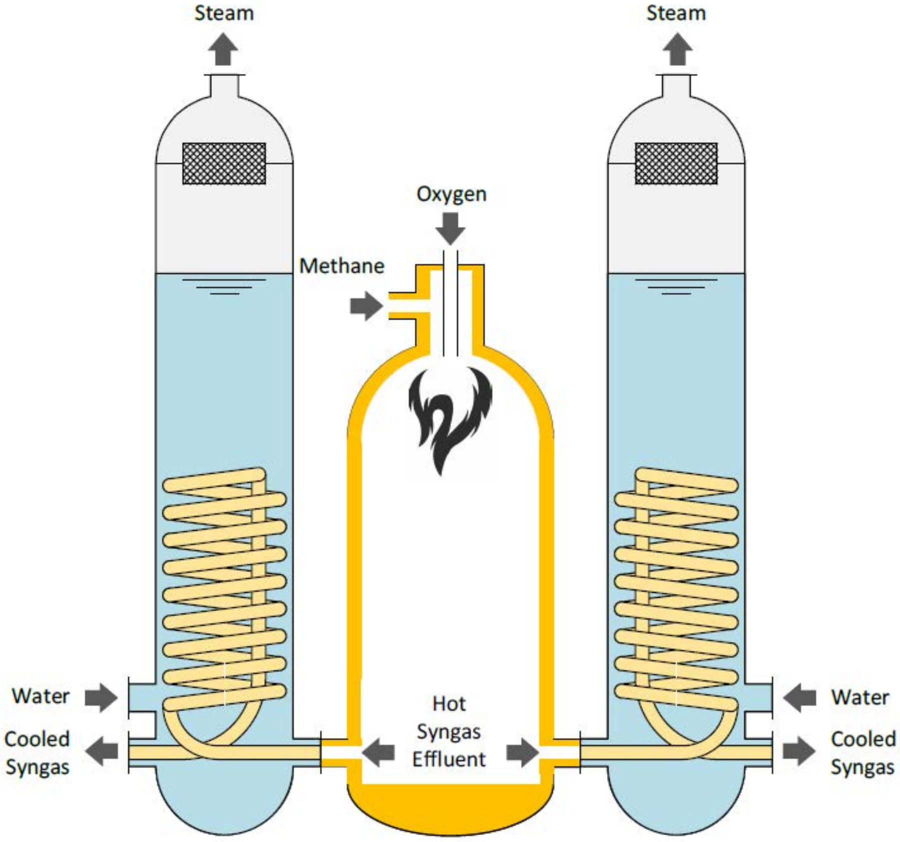
In partial oxidation, methane is first partially oxidised by oxygen to produce hydrogen and carbon monoxide. The partial oxidation reaction is exothermic. The heat produced through the reaction would normally be recovered through the downstream heat recovery process to generate steam from boiler feed water and to preheat other processes to maximise energy efficiency. The chemical reaction occurring in catalytic partial oxidation are shown in Table 17.

Table 17: Partial oxidation and shift technology chemical reactions

Chemical reactions		
Methane partial oxidation	$CH_4 + O_2 \rightleftharpoons CO + 2\ H_2$	ΔH_{298} = -36 kJ/mol
Water gas shift	$CO + H_2O_{(g)} \rightleftharpoons CO_2 + H_2$	ΔH_{298} = -41 kJ/mol
Overall reaction	$CH_4 + O_2 + H_2O_{(g)} \rightleftharpoons CO_2 + 3\ H_2$	ΔH_{298} = -77 kJ/mol

Oxygen required for the partial oxidation reaction is generated through an ASU. Figure 8 shows a typical arrangement in the Shell Blue Hydrogen Process. Feed gas and oxygen is fed at the top of the non-catalytic gas POX reactor, with the syngas from the bottom of the reactor fed to two syngas effluent coolers where reaction heat is recovered to produce high pressure steam.

Figure 8 – Partial oxidation reactor with dual syngas effluent coolers (shell blue hydrogen process)



There are two types of partial oxidation: thermal partial oxidation and catalytic partial oxidation. A key difference between the two types is in the operating temperature and permissible level of sulphur compounds in the feedstock. Thermal partial oxidation occurs at higher operating temperature and can accept higher sulphur feedstocks than the catalytic partial oxidation.

Sulphur can therefore be removed either upstream or downstream of the reactor. Sulphur removal technology and H_2S disposal needs to be considered based on the selected location of the sulphur removal, and the catalyst technology and disposal vs. the alternative of hydrogenation to H_2S, H_2S removal and sulphur recovery.

There is a risk of soot formation, due to partial oxidation (reducing atmosphere) which may depend on the following parameters: feed composition, temperature, pressure, burner design, and flow conditions in the combustion zone [Ref. 3]. In the case of catalytic partial oxidation, the catalyst bed may be selected such that any identified soot precursors are destroyed going through the catalytic bed to avoid soot deposition on the catalyst surface, which would reduce heat transfer. For non-catalytic POX, the amount of soot formation is controlled, and a small amount of soot is typically removed using water wash to protect the downstream equipment.

Syngas from the methane partial oxidation is passed to water gas shift reactor(s), described in section 4.5, operating at optimal conditions to maximise hydrogen production and conversion of carbon monoxide to CO_2 for capture.

4.4. Air separation unit

Oxygen is required for hydrogen production using ATR and POX technologies.

Cryogenic air separation is a mature technology that can produce high volume of oxygen at high purity (>99.5% O_2). The air separation unit (ASU) would include air compression to multiple pressure levels; air drying and purification using temperature swing adsorption; highly integrated multi-stream heat exchange and cryogenic fractionation in a cold box module; expansion of gases in cryogenic turbo expanders; and cryogenic pumping of oxygen [Ref. 19]. The main energy use is in compression of the inlet air.

Using cryogenic air separation, liquid oxygen (and potentially liquid nitrogen) can be produced and stored as a back-up supply.

4.5. CO shift

The syngas stream is fed to the water gas shift reactor(s) to further convert the carbon monoxide into hydrogen and CO_2 through its reaction with excess steam. Considerations to include both high and low temperature or isothermal water gas shift reactors should be taken if higher conversion of carbon monoxide to CO_2 is required.

High levels of shift conversion are usually optimal, particularly where CO_2 is captured from the process and maximising conversion of carbon monoxide to CO_2 leads to higher overall carbon capture. A single shift stage is therefore not usually considered – two shift stages (or isothermal shift) is normal, and three stages may be justified in some cases.

Heat from the exothermic shift reaction can be advantageously recovered into the process or to produce steam. Additional cooling in exchange with ambient air or cooling water is required to cool the shifted syngas further and to remove any free water before the hydrogen purification step.

4.6. CO_2 capture

4.6.1. CO_2 capture locations

CO_2 capture can be achieved at various locations in the hydrogen production process.

With hydrogen production using standard SMR technology, CO_2 capture can be achieved at three different locations:

- process CO_2 capture upstream of the hydrogen purification step

  Approximately 60% of the total CO_2 from the process is present in the shifted syngas at this point (the balance of the CO_2 being in the reformer flue gas from combustion of methane and carbon monoxide in the fuel gas). As near full CO_2 removal can be achieved from the stream, the overall CO_2 capture rate is approximately 60% [Ref. 10].

  This location minimises CO_2 capture cost, but limits CO_2 capture rate. For retrofit of CO_2 capture on existing SMR plants, this may be a viable option.

- CO_2 capture from the tail gas produced in the hydrogen purification step

  Again, up to approximately 60% of the total CO_2, assuming no process CO_2 capture upstream of hydrogen purification.

  CO_2 capture from the hydrogen purification tail gas is a demonstrated alternative to capture upstream of hydrogen purification. Advantages are that the stream is concentrated in CO_2, which suits some capture technologies, and that loss of operation due to trip of the CO_2 capture unit does not impact hydrogen production, as CO_2 is separated from hydrogen in the hydrogen purification (PSA) system and captured downstream,.

  Disadvantages are an increase in sizing of the hydrogen purification system and recovery from a low pressure tail gas stream.

- post-combustion CO_2 capture from the reformer flue gas outlet

  On top of the approximately 60% of the CO_2 produced in the process, this location gives the opportunity to capture and the remaining 40% of the CO_2 resulting from combustion of carbon monoxide and hydrocarbons in the fuel gas.

The advantages of combining process CO_2 capture and post combustion capture are limited, particularly as high CO_2 capture rates of > 95% should be achievable post-combustion. A single capture step would therefore be simplest, with CO_2 removed from the process in the hydrogen purification step (PSA unit), and routed with the tail gas used as fuel, with all CO_2 captured post-combustion from the flue gas.

Table 18: CO_2 capture locations and associated capture rate for SMR

CO_2 capture locations	CO_2 capture from stream (%) [Ref. 10]	Overall CO_2 capture rate (%) [Ref. 10]
Shifted syngas, upstream of hydrogen purification	~ 100	60
PSA tail gas, downstream of hydrogen purification	~ 100	60
Post-combustion, from flue gas	> ~95	>~ 95

With ATR and POX technology (also SMR if hydrogen rich fuel is used), CO_2 capture objectives can be met by maximising conversion of methane to CO_2 and hydrogen (including through the addition of a GHR step to increase reforming) and optimising CO shift sections, enabling process CO_2 capture from the hydrogen product stream, with no requirement for post-combustion capture:

- process CO_2 capture upstream of the hydrogen purification step. This stream will contain approximately 25 mol% CO_2 at high pressure. CO_2 removal efficiency of close to 100% from the stream should be expected using amine solvent
- process CO_2 capture from the tail gas from the hydrogen purification step. Capture from this location increases load on the hydrogen purification step, with capture from a low pressure stream containing typically greater than 70 mol% CO_2, based on no CO_2 capture upstream of the hydrogen purification step

Overall CO_2 removal rate is proportional to the degree of upstream conversion to CO_2. Carbon in the form of methane or carbon monoxide will either pass with tail gas from hydrogen purification (to fuel gas pre-heating in an ATR process) or will pass to the hydrogen product if the required hydrogen purity specification allows methanation to convert carbon monoxide to methane rather than removal.

An overall CO_2 removal rate of around 97% is expected to be achievable, where any fuel gas demands for process heating or steam generation can be met by hydrogen purification tail gas or hydrogen product rather than combustion of feed gas. [Ref. 10].

With POX hydrogen production technology, there is not typically a need for auxiliary fired equipment, and therefore no requirement for fuel. If purification of the hydrogen product is achieved through pressure swing adsorption, this will produce a tail gas stream, as shown on Figure 5, which becomes a by-product, not used within the hydrogen production process. This may be used as fuel elsewhere, and the considerations for the combustion of this fuel stream would be similar to those if it were used as fuel in the process, with decarbonisation objectives achieved through high conversion rates and CO_2 capture in the upstream process. If purification of hydrogen product is achieved through methanation, there is no tail gas resultant from the process, and an overall CO_2 removal rate of >99% can be achieved within the installation, although carbon monoxide converted to methane and remaining in the hydrogen product will form CO_2 on combustion of the product at the point of use.

Post-combustion capture from flue gases from combustion of fuel with low carbon content, such as hydrogen purification tail gas may not be feasible, and any small incremental benefit in increased CO_2 capture rate are likely to be outweighed by the energy use, additional risks (including environmental impacts) and costs introduced by the addition of a post-combustion capture system.

4.6.2. Process CO_2 capture

The shifted syngas is fed at high pressure to a CO_2 capture unit, where CO_2 is separated from hydrogen. The CO_2 capture unit produces a CO_2 rich gas, which is compressed to the pressure required for export from the site. Downstream of compression, or at an optimal pressure within the compression train, the CO_2 is dehydrated and treated as necessary to meet the export specification.

Process CO_2 capture technologies include[12]:

- state of the art chemical solvent absorption technologies, predominantly amines
- physical solvent absorption
- low temperature (cryogenic) bulk CO_2 separation, relatively novel in the context of large scale hydrogen production, and requiring combination with other CO_2 capture technologies, but with potential to capture a portion of the CO_2 without the heat requirement for solvent regeneration and with the ability to deliver CO_2 at higher pressure than solvent absorption processes, reducing downstream compression requirements.

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[12] The most commonly used chemical, physical, and cryogenic solvents are listed in Section 3.2. Information about each solvent can be directly found in the technical review completed by IEAGHG [Ref. 10].

The International Energy Agency Greenhouse Gas R&D Programme (IEAGHG) evaluated the process CO_2 capture rate for alternative CO_2 capture technologies from both shifted syngas and PSA tail gas in an SMR hydrogen production plant. The study concluded process CO_2 capture of PSA tail gas using MDEA and cryogenic + membrane separation were comparable, with their overall CO_2 capture rate being 54% and 53% respectively [Ref. 8]. This is also comparable to the CO_2 capture rate quoted in section 4.6.1.

- vacuum swing adsorption (VSA)

Vacuum swing adsorption (VSA) is a novel CO_2 capture technology which has been implemented at Air Products' Port Arthur hydrogen production facility in 2013 and is the first commercial scale SMR with VSA CO_2 capture [Ref. 5]. A key reason that VSA technology was selected at Port Arthur over the alternative of chemical solvent absorption was the additional steam requirement to regenerate the amine solvent, which was, in that case, a significant energy burden on the system and difficult to accommodate [Ref. 5].

Various independent studies have been conducted on CO_2 capture in hydrogen production, considering different hydrogen production technologies, CO_2 capture technologies and locations. VSA CO_2 capture technology was assessed in studies by the Royal Society of Chemistry [Ref. 9] and by Industrial & Engineering Chemistry Research (I&EC Research) [Ref. 14, 15].

4.6.3. Post-combustion CO_2 capture

Chemical absorption is the most suitable technology for post-combustion CO_2 capture due to the flue gas conditions, for example, low pressure and low CO_2 concentration. Such post-combustion CO_2 capture uses a recirculating chemical solvent, typically an amine solution, which reacts chemically with the CO_2 at in an absorber tower, with the reaction reversed at elevated temperature in a regenerator tower to release a concentrated CO_2 stream. It includes the following main steps:

- **Flue gas conditioning** – Cooling of the flue gas, typically by direct contact with recirculating cooled water in packed tower. It may also be necessary to boost the pressure of the flue gas using a fan / blower, to provide sufficient pressure to overcome the pressure losses through the system, but this would be dependent on the application. Pre-treatment to remove contaminants such as NOx may also be necessary, for example, with selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR), particularly considering potential of these contaminants to react with amine solvents producing degradation products.
- **CO_2 absorption** – Flue gas from the direct contact cooler is passed to an absorber tower containing packing in which CO_2 is absorbed in counter-current contact with the

amine solvent. There may be a requirement for inter-cooling within the absorber system. After CO_2 capture, the flue gas passed through a water wash section to remove any droplets or volatile solvent before being discharged to atmosphere. The wash water section also allows control of the flue gas temperature and water balance to reduce water make up needs. The decarbonised flue gas will leave the water wash section at relatively low temperature, saturated with water, and the impact on dispersion characteristics and visible plume formation need to be considered.

- **Solvent regeneration** – Solvent, rich in CO_2, from the base of the absorber tower is pumped to a regeneration system. Heat is exchanged with hot lean solvent, increasing the rich solvent temperature and reduce external heating and cooling requirements for regeneration. The rich solvent is fed to a regeneration column which includes a stripping section below the feed, in which solvent is contacted with water vapour produced by a reboil system, at the column base. The column also includes a rectification section above the feed, in which the vapour, carrying the CO_2 is contacted with water produced by an overhead condenser and reflux system. A concentrated CO_2 stream is produced from this overhead system, suitable for routing to CO_2 compression system. In some proprietary processes, additional features are included for heat recovery and efficient solvent regeneration. Amine solvents react with some flue gas components to produce heat stable salts and other by-products, levels of which need to be controlled by bleeding off a portion for processing to reclaim the solvent.
- **Lean solvent** – Lean solvent from the regeneration system is pumped, cooled, and circulated to the CO_2 absorber tower. A lean solvent storage tank is normally incorporated to provide buffer storage. As amine solvents react with oxygen and other contaminants in the flue gas, there is a need for thermal reclamation to maintain solvent quality, in which a slipstream of lean solvent, containing degradation products including heat stable salts, is fed to a reclaimer unit. This is typically a column operating at high temperature, from which water and solvent can be distilled, leaving a residue containing the separated degradation products for disposal off-site.

For SMR hydrogen production technology, post-combustion CO_2 capture is required from the flue gas at the SMR furnace outlet (Fig.3). For ATR hydrogen production technology, post-combustion CO_2 capture may be an option for auxiliary fired heaters / boilers, although the use of low carbon content fuel such as hydrogen purification tail gas make this unlikely to be optimal (Fig.4). CO_2, CO, and methane in the hydrogen purification tail gas should be kept as low as practical to minimise CO_2 in combustion products when the tail gas is used as a fuel source elsewhere in the process.

4.7. Hydrogen purification

Hydrogen product from the CO_2 capture unit can be further purified in a hydrogen purification unit before being compressed (if necessary) to the pressure required for downstream distribution / use.

This process step primarily removes unreacted carbon monoxide from the hydrogen product, but also other components requiring removal to meet the process specification – for example, methane, CO_2 and nitrogen. In modern conventional hydrogen production plants, all hydrogen purification, including CO_2 removal is undertaken in the PSA unit.

Technologies may include pressure swing adsorption (PSA) and/or a methanation step to convert any residual carbon monoxide to methane in the final hydrogen product stream, as long as the methane content still meets the hydrogen specification. Methanation is an exothermic reaction that takes place at 300°C in a reactor filled with a nickel-based catalyst. The chemical reactions occurring in methanation are shown in Table 19.

Table 19: Methanation chemical reactions

Chemical reactions		
Methanation (1)	$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	$\Delta H_{298} = -206$ kJ/mol
Methanation (2)	$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$	$\Delta H_{298} = -165$ kJ/mol

Some of the hydrogen is used in producing methane (which has calorific value) and water (which does not).

Any heat produced through the reaction would typically be recovered through a feed / product interchanger to maximise energy efficiency. The temperature rise over the methanation reactor is normally small due to the relatively low levels of CO and CO_2 in the feed to the unit.

PSA introduces a relatively small loss of hydrogen with the tail gas, but this is in any case normally used as fuel within the process, and this can help meet overall heat balance for a SMR reformer furnace or auxiliary heaters or boilers in ATR processes.

4.8. Heat and condensate recovery

The cooling of the syngas stream leaving the reforming process and the exothermic CO shift reaction generate heat and steam, which may be recovered through a waste heat recovery process to integrate with other processes (for example, solvent regeneration in the carbon capture step and/or hydrogen purification step or to preheat boiler feed water) and maximise energy efficiency.

Process condensate resulting from steam condensation is normally recovered and reused after necessary treatment to remove any residual impurities such as methanol, ammonia etc. The process condensate may beneficially supplement boiler feed water supply in the steam generation system or used elsewhere in the process.

4.9. Power

A co-generation unit might be implemented to assist steam and power supply to the hydrogen production / CO_2 capture process and may also enable any surplus steam and power production for export. The addition of a co-generation plant to the hydrogen production and carbon capture processes may improve the overall energy efficiency of the plant while reducing the overall impact to the environment, for instance, were it to be fuelled with a portion of the hydrogen product gas.

A standalone SMR without CO_2 capture may produce excess steam, which is typically exported to industrial users. With addition of post-combustion capture, the excess steam can be used to generate power via a steam turbine, with the resultant low pressure steam used to provide heat required for the CO_2 capture solvent regeneration. The power produced can be used to satisfy all of the overall stand-alone unit's power requirements for pumping, compression, etc. With inclusion of a convective reformer (GHR), the process can be balanced in terms of steam production and demand.

For an ATR with CO_2 capture, the CO shift and cooling of the process gas will generate excess steam which can be used to produce power and part supply the plant power requirement. With inclusion of a convective reformer (GHR), the process can be balanced in terms of steam production and demand.

For the POX process with CO_2 capture, excess steam is produced which can be used to generate power, again part supplying the plant power requirement.

Hydrogen production may be integrated with co-generation to improve energy efficiency, operational flexibility and to minimise impact to the environment, with the potential for higher thermal efficiency [Ref. 5].

5. Environmental considerations and guidance

Although it is recognised that hydrogen production technology will be selected considering a range of commercial, technical, and economic factors, the selection of technology and plant configuration should account for the environmental performance, considering energy efficiency, resource use, and impact on CO_2 capture methods and performance.

Another key consideration is on the requirement for electrical power to support the process. SMR processes, for example, can typically produce an excess of high pressure steam, used to generate power or drive mechanical equipment and produce low pressure steam for CO_2 capture solvent regeneration. The main power demands in this case are in CO_2 capture and compression. Other hydrogen production processes such as GHR + ATR may consume less feed gas, but do not have the same excess of high pressure steam to produce power, and have additional power demands for production of oxygen. The source of electrical power supply is an important consideration, but the carbon intensity of imported electrical power is outside the scope of this assessment.

5.1. Feed gas supply

Depending on the source of feed gas to the process, it will meet gas network entry or local refinery fuel gas specifications, with limitations on sulphur, mercury, and heavy hydrocarbon content.

Any CO_2 in feed gas will be removed later in the process, together with CO_2 produced in the hydrogen production process. Nitrogen in feed gas may also require removal from the hydrogen product in the hydrogen purification process to meet hydrogen inert content specification, depending on the quantity in the feed gas.

The range of composition is important for example in order to specify the desulphurisation and pre-reforming stages. The full compositional range should be specified, particularly in the case of refinery fuel gases which can typically be from several sources.

Sulphur (SO_2) emission sources to air (through combustion of fuel gas) should be limited through the use of a low sulphur feed gas or by pre-treating the feed gas to remove the sulphur-containing species.

5.2. Feed gas desulphurisation and pre-reforming

Feed gas treatment depends on feed gas contaminants, sensitivity of reforming and CO shift catalysts to poisoning and deactivation, and hydrogen product specifications. Technologies for sulphur removal and mercury removal are described in section 4.1.

This is typically achieved through hydrogenation of sulphur containing compounds and their removal on a catalyst adsorbent. As such technology is suitable for trace removal, where possible, the removal of sulphur components from the feed gas to the hydrogen production process should be maximised in upstream facilities to avoid excessive use of adsorbent catalyst, requiring disposal / recycle.

Catalyst selection should be made considering environmental performance, accounting for:

- any required pre-treatment to avoid poisoning, to minimise waste and associated treatment
- prevention of any dust emissions, where applicable
- ability to recover/recycle the solids/metals from the spent catalyst waste
- handling of spent catalyst for environmentally safe recovery / recycling / disposal

Requirements for pre-reforming, in which ethane and heavier hydrocarbons are broken down at a relatively low operating temperature, to avoid production of carbon residues in the methane reforming step, are also specific to the feed gas source and composition. In the adiabatic pre-reformer, endothermic reforming reactions convert heavier hydrocarbons and some of the methane to CO and hydrogen, while exothermic CO shift and methanation reactions will also reach equilibrium, giving a mixture of methane, CO_2, carbon monoxide and hydrogen to the downstream reformer.

As the pre-reforming step transfers reforming duty out of a SMR, it allows a reduction in the reformer size and fuel gas consumption. Incorporation of a pre-reforming step can therefore be considered, to optimise the overall environmental performance, for example to optimise energy efficiency and to minimise NO_x emissions to air. In increasing the degree of pre-reforming, consideration needs to be given to the steam balance for reforming with CO_2 capture, and steam required for the steam turbine and CO_2 capture solvent regeneration reboiler. Where the feed gas is low in heavier hydrocarbons, for example, where the gas is processed upstream for recovery of natural gas liquids, there may be little or no advantage in pre-reforming.

5.3. Reforming and CO shift

In the reforming and CO shift sections, methane conversion to hydrogen, carbon monoxide and CO_2 minimising methane slip, and the carbon monoxide conversion to CO_2 should be optimised considering the overall CO_2 capture target, and the impact on downstream processing to meet the hydrogen product specification.

In the case of oxidation reactions in the process, equipment design, and operating parameters should be optimised to minimise risk of soot formation. In the case of autothermal reforming, the potential to destroy any identified soot precursors in the catalyst bed to avoid soot formation should be considered (reference earlier section 4.3.2). The need for soot removal, for example, in the case of non-catalytic partial oxidation with high operating temperatures, to protect downstream systems is to be considered, along with disposal requirements.

CO shift technology selection should consider the environmental performance:

- to maximise energy efficiency, particularly through best heat integration with the overall hydrogen production and CO_2 capture processes
- to minimise the duration of start-up operations and associated emissions to air from flaring
- to minimise production of wastes

A single step CO shift process may be considered in place of a more conventional high temperature / low temperature shift process, with isothermal conditions achieved through reactor cooling with recovery of heat. A key driver for this is in overall heat integration and efficient use of recovered heat, as long as sufficient conversion of carbon monoxide to CO_2 is achieved. This also avoids use of chromium catalyst needed for high temperature shift, minimising waste, and reduces potential for catalyst damage, methanation reactions, and Fischer-Tropsch reactions (for example, producing methanol which would condense with the water downstream), which can occur in high temperature shift processes if the steam to carbon ratio is too low [Ref. 1].

As high steam to carbon ratios will be employed in any case, to maximise CO_2 conversion and capture rates, risk of over-reduction of catalyst is low, and the benefits of the isothermal reactor will be weighed up by the designer against the requirement for a more complex multi-tube boiling water cooled reactor.

Methods for environmentally safe disposal and recycle / recovery of catalyst materials, should be addressed.

5.4. Process CO_2 capture from hydrogen product

Technology for CO_2 capture from the hydrogen product stream will typically be through absorption in a circulating chemical solvent, with regeneration of the solvent through reduction of pressure and heating to liberate CO_2.

The solvent should be selected, and parameters optimised within CO_2 removal system, to maximise energy efficiency and capture performance:

- lean solvent conditions and absorber system design for high degree of CO_2 capture to meet overall carbon capture objectives and reduce load on downstream hydrogen purification
- operation of regeneration system to deliver CO_2 at as high a pressure as practical (with pressure limited by operating temperature considerations to avoid excessive degradation of solvent), and avoidance of excessive pressure loss in CO_2 product system, to reduce CO_2 compression power requirements
- optimisation of lean/rich solvent heat exchange to reduce reboiler heat requirements for solvent regeneration

Consider technologies which reduce heat requirements for solvent regeneration, such as producing a semi-lean solvent stream for bulk removal in the bottom section of the absorber. Such techniques increase overall solvent circulation and pumping requirements but reduce heat requirements for full thermal regeneration of the solvent.

Consider technology which allows recovery of CO_2 at higher pressure, for example, solvent systems with flash regeneration of a portion of CO_2 at intermediate pressure, the benefits of which are dependent on the operating pressure of the reforming process and CO_2 absorber.

Absorber design should minimise carry-over of solvent, for example, through water wash and/or demisting, to minimise impact on the downstream hydrogen purification process and associated product and off-gas streams.

The overhead condenser / reflux system and section above the feed on the solvent regeneration column will minimise potential for solvent to reach the CO_2 product. Requirements for continuous purge from the reflux system to avoid build-up of components such as methanol which may be co-produced in the hydrogen production process should be considered, such that this can be managed within effluent treatment facilities.

Consider low temperature bulk separation of CO_2, with condensation and separation of a portion of CO_2 for delivery at elevated pressure. This has potential to reduce load on the downstream solvent-based system, and its associated heat requirements, and also reduce CO_2 compression requirements. Pre-treatment of feed gas to a low temperature separation will be required to remove water which would otherwise freeze in the process.

Requirements for CO_2 venting when downstream systems are not available should be considered, including requirements for an elevated local vent stack designed to optimise dispersion. Potential for atmospheric emission of solvent or associated substances should be low in such circumstances, but measures taken to mitigate this, such as ensuring continued operation of the regenerator overhead condenser and reflux system, should be identified.

Continuous CO_2 venting should not be planned as a normal operating mode, but rather when required in transient operation for control and to avoid wider disruption of the process, or when required temporarily in emergency operation. Where venting is required from high pressure CO_2 systems, where there is a significant cooling effect on pressure reduction, the measures taken to ensure adequate atmospheric dispersion should be identified.

5.5. CO_2 capture strategies specific to steam methane reforming

In the steam methane reforming process, process heat is provided by external combustion in a reformer furnace. Typically, a portion of the feed gas is used as fuel, with the majority of energy supplied from off-gas from hydrogen purification. Use of hydrogen, taken either before or after purification, is a potential alternative to use of feed gas as fuel. Otherwise, post-combustion capture is required to avoid the CO_2 emissions from combustion of hydrocarbons in the reformer as described below.

Within the SMR process, there is a need to remove CO_2 from the hydrogen product stream to meet the hydrogen quality specification. This can be achieved in two ways, and the optimal approach should be justified:

1) CO_2 removal combined with the hydrogen purification step, with for example a pressure swing adsorption unit delivering the CO_2 with the other impurities removed in an off-gas stream used together with feed gas to fuel the reformer furnace.

In this case, all carbon containing components from the syngas will be present as CO_2 in the flue gas from the reformer furnace and require post-combustion capture.

2) CO_2 removal upstream of the hydrogen purification system, with for example a solvent based CO_2 removal system, separate to other impurity removal from the hydrogen product.

In this case, near full removal of CO2 from the process stream can be achieved, with the carbon in the off-gas from the purification step (assuming pressure swing adsorption) limited to any methane and carbon monoxide slip from the upstream reforming and CO shift reactions.

With the conventional use of PSA tail gas (containing carbon monoxide) combined with feed gas to fuel the reformer furnace, post-combustion capture would still be required, with the difference made by upstream removal of CO_2 being mainly the impact on overall energy use for CO_2 capture, and the overall impact on hydrogen purification and CO_2 capture equipment sizing.

Given there are practical and economic limitations to the percentage post-combustion capture of CO_2, overall percentage CO_2 capture may be increased slightly by reduced reliance on the post-combustion capture step. However, with a 95% CO_2 capture rate potentially achievable in post-combustion capture from SMR flue gas [Ref. 6, 21], the increase in capture rate is small. Therefore, it is likely that applying post-combustion capture only, without a dedicated process CO_2 removal step upstream, will be the most economic option for achieving high CO_2 capture rates for most SMR-only based projects.

Together with use of hydrogen to fuel the reformer furnace, process CO_2 removal may avoid the need for post-combustion capture while meeting CO_2 capture objectives. In this case, the hydrogen production process would require capacity to produce both hydrogen product and hydrogen fuel gas. Any associated impacts of using fuel with higher hydrogen content on the SMR burners, and on NO_x formation in the reformer furnace would also need to be confirmed.

5.6. Post-combustion CO_2 capture from SMR furnace flue gas

Where post-combustion capture of CO_2 is employed, capture of 95% of the CO_2 from the flue gas is possible, and it expected this this will be maximised within practical and economic limits, with capture of greater than 95% potentially feasible [Ref. 6, 21].

In order to reduce emissions of CO_2, or polluting substances such as volatile components of the amine solvent and likely degradation products such as nitrosamines and nitramines to air, the post-combustion CO_2 capture system must be designed with high availability and with flexibility to handle expected variation in flue gas flow and conditions.

A guidance document for post-combustion capture (PCC), specific to CO_2 capture using amine solvents for power and CHP plants fuelled by natural gas and biomass, has been developed in parallel and independent of this guidance [Ref. 6, 21] and should be referred to for further information.

There are some differences in flue gas composition resulting from combustion of hydrogen rich fuel gas and natural gas in the reformer furnace, and the flue gases considered in the PCC guidance. Gas turbines for example operate with significant excess air for temperature control and the CO_2 is more dilute with higher oxygen and nitrogen content in the flue gas. Combustion of hydrogen rich streams can however give rise to high NO_x formation, and guidance provided on reaction of amine solvent with NO_x, and the requirements in some cases for upstream NO_x removal is relevant.

Start-up and shut-down operations are expected to be less frequent and hence a lesser consideration for hydrogen production from methane than for example in dispatchable power generation applications where post-combustion capture is also being considered. The requirements however for ramp-up and ramp-down of hydrogen production on CO_2 capture and environmental performance need to be considered.

Key environmental considerations to be addressed in the design of post-combustion capture from reformer furnace flue gas include:

- solvent selection, reflect the balance between CO_2 capture performance, associated energy requirements and potential atmospheric emissions, such as:
    - energy requirements for circulation and regeneration of amine solvent
    - reclaiming potential, to manage solvent quality and handle contaminants, removing degradation products including heat stable salts
    - potential for reaction with contaminants in flue gas, and impact on requirements for upstream conditioning of flue gas, for example, for NO_x removal
    - potential atmospheric emissions of solvent and associated degradation products such as nitrosamines and nitramines
    - proven performance through operational experience, or test programmes under realistic operating conditions
- atmospheric emissions, considering:
    - emissions of solvent components
    - emission of additional substances formed in the CO_2 capture system such as nitrosamines, nitramines and ammonia
    - emission of ammonia present in flue gas though slippage from upstream NOx removal
    - formation of further additional substances in the atmosphere from those emissions
- energy requirements:
    - heat – for example, low pressure steam for amine regeneration, with higher grade heat only for thermal reclaiming

  - power – for example, for pumping of amine and water streams; compression of flash vapour if applicable; and for flue gas fans / blowers which given large volumetric flows can add significantly to power requirements
- effluent streams:
  - the main effluent will be from purge of water condensed in cooling the incoming flue gas, in which any expected pollutants will need to be identified
  - potential for water to be recovered and reused within the process should be assessed
- all wastes requiring recycling or disposal must be identified, including:
  - waste from thermal reclaiming of amine solvent
  - solid wastes such as from amine filtration
- flue gas delivery and cooling requirements:
  - the process and layout should be designed to minimise requirement for flue gas fans / blowers which introduce additional power requirements, noise, and impact on availability. This will be particularly important where there are additional constraints in retrofit applications
  - flue gas cooling will typically be thorough direct contact with water in a packed tower, with the circulating water cooled against air or cooling water. Condensation of water from the flue gas will require continuous purge from the circuit. Impact of any water carryover from the direct contact cooler on the downstream CO_2 removal system, such as contamination of the amine solvent, should be assessed, with measures incorporated to eliminate carryover of water droplets as appropriate
- avoidance of excessive pressure drop through the flue gas cooling and absorber system
- flue gas contaminant removal for effective operation of the capture system should be identified:
  - SO_2 – typically managed through removal of sulphur to very low levels upstream of hydrogen production, and potential to remove in combination with direct contact cooling to be considered if required
  - NO_x – as this has potential to form stable nitrosamines with some solvents, upstream removal may be required, depending on the selected solvent
  - expected levels of contaminants in flue gas will need to be identified for the specific fuel gas composition and combustion conditions, considering use of feed gas, hydrogen purification off-gas or hydrogen product as fuel, in conjunction with proposed burner technology and combustion air flow
- absorber outlet conditioning, including:
  - design of wash sections, typically using water, to capture droplets of solvent and volatile components. This will typically control overall water balance with recovery of solvent into the process

  - once available emissions reduction techniques have been incorporated, consider the need to heat flue gases from the absorber to improve dispersion, for example through heat exchange with hot flue gas upstream of the direct contact cooler, and the impact this has on any additional heat requirements, flue gas pressure balance and need for fans / blowers to boost flue gas pressure

5.7. CO_2 capture rate

A design CO_2 capture rate of 95% or greater is expected to be achievable for the hydrogen production and CO_2 capture routes considered for new plant:

- for SMR hydrogen production with post-combustion capture, this is consistent with expectation for CO_2 capture using amine-based technologies for power and CHP plants [Ref. 6, 21]
- for ATR with GHR, SMR with GHR, or POX hydrogen production processes, the 95% or greater CO_2 capture rate is dependent on high conversion of the methane to CO_2 through the reforming and CO shift sections, and near full removal of CO_2 from the hydrogen product, both of which are considered feasible

If a design CO_2 capture rate of less than 95% is proposed, justification will need to be provided by the applicant. For retrofit applications, there may be additional limitations on achievable CO_2 capture rate due to the constraints presented by existing facilities.

In operation, the actual CO_2 capture rate may vary, depending on the operating regime.

Decarbonisation readiness and future proofing

This applies to England and Wales only. It does not apply currently to Scotland and Northern Ireland.

There was a call for evidence by BEIS and the Welsh Government on decarbonisation readiness from July to September 2021.The government is currently analysing the results (correct as of July 2022).

Decarbonisation readiness: call for evidence on the expansion of the 2009 Carbon Capture Readiness requirements - GOV.UK (www.gov.uk).

The consultation includes the proposal that the requirement for all combustion processes (with no de minimis) to be decarbonisation ready be included in the Environmental Permitting Regulations (England and Wales) 2016.

There are some streams, for example, the flue gases from combustion of residual (tail) gas from the hydrogen purification process with a relatively high CO_2 concentration which may need to be decarbonised in future and should therefore be made decarbonisation ready by maintaining the necessary space and technical retrofit capability for future carbon capture.

Carbon in hydrogen product

It is noted that any CO, CO_2 or CH_4 or other carbon containing compounds as allowed by the product specification in the hydrogen product will be emitted to the environment as CO or CO_2 (assuming that the hydrogen product enters a combustion process at its point of use and that the carbon-containing compounds undergo conversion during combustion to CO or CO_2).

Reporting of CO_2 emissions from imported electricity production

The source of imported electricity and any associated CO_2 emissions are not in scope of the permitting assessment for an IED installation.

These emissions are accounted for elsewhere in the energy system. [Ref. 23].

5.8. Hydrogen product purification

Hydrogen purification requirements will depend on specified hydrogen product quality and impurities present following reforming, CO shift and CO_2 capture steps.

It will be necessary to consider:

- nitrogen and argon – present in feed gas or oxygen supply
- methane – which is not converted to carbon monoxide in the reforming section
- carbon monoxide – which is not converted to CO_2 in the reforming or CO shift sections
- CO_2 – which is not removed in the CO_2 capture section
- water – with the hydrogen stream saturated with water following CO_2 capture

Where the hydrogen product gas specification allows, and particularly where it is intended the hydrogen is blended with methane for downstream distribution, methanation (conversion of carbon monoxide to methane) could be considered as an alternative to separation of impurities. In this case, it is likely there will remain a requirement for dehydration to meet moisture specification, with methanation reaction introducing additional water.

Shutdown procedures for methanation reactors to prevent formation of toxic nickel carbonyl from reaction of CO with the nickel catalyst at lower temperatures will need to be employed in line with operating experience and established procedures.

Where hydrogen is produced with the intention of blending externally with natural gas, the impact of blending on the overall specification should be considered, with dilution of impurities, and ability to relax hydrogen purity to enhance energy efficiency and reduce / eliminate production of low pressure / low calorific value off-gas streams.

5.9. Off-gas production from hydrogen purification

Off-gas produced from hydrogen purification will be rich in hydrogen (from depressurisation and purge of the adsorber vessels) and will contain nitrogen from feed gas, argon from oxygen supply, and any methane, CO, and CO_2 that is not converted / removed upstream. The off-gas is normally used as fuel gas.

In the case of SMR with post-combustion capture, the amount of methane, carbon monoxide and CO_2 slip with the off-gas is largely an economic decision, as feed gas, containing carbon, is in any case introduced as supplementary fuel to the reformer furnace to satisfy heating requirements. There is an argument for avoiding high levels of methane or carbon monoxide slip through the process, as this increases the amount of gas being processed, however the optimum conversion rates may be lower than in other processes. Conversion rates in the process should be optimised considering environmental impacts of excessive slip of methane or carbon monoxide, such as on overall energy use.

In the case of processes with ATR or POX reactions, which do not employ post-combustion capture, slip of methane or carbon monoxide from the reforming and CO shift stages removed in hydrogen purification will end in the off-gas used as fuel and hence will represent uncaptured CO_2. Conversion rates in the process should be optimised to meet CO_2 capture objectives balanced with other environmental performance factors, such as overall energy use.

For POX based hydrogen production, there is potentially no requirement for combustion in auxiliary boilers or fired heaters, and off-gas produced from hydrogen purification is not required to meet the fuel balance. In this case, a use for the off-gas outside of the hydrogen production facility would need to be found, or the hydrogen production facility design adapted to utilise the off-gas for generation of heat or power, for example, in superheating of the steam generated in the process.

5.10. Heat integration and process cooling

Within the hydrogen production process, heat integration will typically be through gas / gas exchange, including in gas heated reformer where used; or through heat recovery for steam generation and superheating, including demineralised and boiler feed water heating.

Heat recovered through process cooling downstream of the reforming section, to condition the temperature for CO shift reaction, is at high grade and can be used for both direct heat integration within the process and producing steam at higher pressure levels for use in the process.

Heat recovered in condensation of water downstream of the CO shift reactor will be at lower grade, but at suitable temperature for use in CO_2 capture process using amine solvents. Recovery should be optimised through a suitable medium such as low pressure steam, or through direct heat transfer with syngas, to suit the CO_2 capture process, thus providing an opportunity for improved overall thermal efficiency.

There will ultimately be a need to cool further against ambient air or cooling water, but opportunities should be maximised to use the heat, for example in heating demineralised and boiler feed water.

Selection of ambient cooling medium – for example, air cooling, indirect sea water cooling, open (evaporative), closed or hybrid cooling circuits – should account for any impact of cooling temperature on process performance or energy efficiency, such as intercooling temperature on power requirements for compression.

Where the hydrogen production process has potential to produce excess high pressure steam, consideration should be given to how this is used most efficiently to generate electrical power or drive mechanical equipment such as compressors within the process. Heat integration to make best use of lower grade heat, as described above, may provide additional opportunities for more optimal use of high pressure steam.

Regarding heat recovery from CO_2 compression, the following references are relevant for heat recovery options from CO_2 compression trains.

These indicate that there is potential for at least 22% of compressor electrical power input to be recovered via cooling water from multi-stage compressor intercoolers and use of organic rankine cycle.

See [Ref. 24] p. 11 final paragraph of section 4, which also references [Ref.25].

5.11. Combustion

Requirements for fired equipment to provide heat to the process and generate steam is dependent on the reforming process. It can present a practical means of disposal of low pressure off-gas stream from hydrogen purification, for example using tail gas from a pressure swing adsorption process as fuel and balancing overall process heat requirements. It introduces a source of atmospheric emissions.

For steam methane reforming, external combustion in the reformer furnace represents a significant source of atmospheric emissions, with heat requirements typically provided through combustion of a portion of the feed gas together with off-gas from hydrogen purification. In this case, management of combustion emissions should be considered alongside those relating to post-combustion CO_2 capture.

In the case of autothermal reforming, where the majority of heat is provided by reaction with oxygen within the process, there is a lesser requirement for heat from auxiliary furnaces or boilers and it is most likely that this can be satisfied by combustion of hydrogen rich off-gas streams or hydrogen product.

In the case of partial oxidation, no furnaces or boilers are required, and combustion products are not normally produced.

Hydrogen combustion produces higher flame temperatures than methane combustion and has potential for higher thermal NO_x formation from reaction of nitrogen and oxygen.

Where hydrogen or hydrogen enriched fuel gases are combusted, techniques to control flame characteristics and reduce NO_x formation should be considered. This may include specially designed burners, flue gas recirculation or heat exchange with fuel/air.

Variation of fuel gas composition, particularly hydrogen content, needs to be considered, including any requirements to switch between fuel gas sources. Start up and shut down operations should be considered, as PSA tail gas will not be available for example when the plant is ramping up to minimum flow, and any fuel will be taken from methane feed.

Other established techniques such as selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) may need to be considered if NO_x formation in combustion gases cannot be reduced to acceptable levels, considering environmental risk to air quality and any prescribed emissions limits.

The emission levels for the combustion equipment in the scope of the hydrogen production and CCS plant will need to be identified from the existing sources of statutorily applicable emission limits, including the following:

- Medium Combustion Plant Directive
- Industrial Emissions Directive, Annex V
- BAT conclusions and BRef for the refining of mineral oil and gas
- BAT conclusions and BRef for large combustion plant
- BRef for large volume inorganic chemicals (ammonia and fertilisers)

This in accordance with the type of combustion equipment, fuels proposed to be combusted, net rated thermal inputs, Best available techniques for control of emissions, and the conclusions of an environmental risk assessment, considering the dispersion of pollutants into air and the sensitivity of the relevant receptors.

The regulators will take a case by case decision on the applicable emissions limits, based on the elements outlined above and the most apt reference source of emission limits.

Given that supply of oxygen is required for some hydrogen production processes, additional oxygen production to support oxy-combustion may be considered. Removing the source of nitrogen from combustion air would avoid NO_x formation, but experience in design and operation of such combustion systems is limited, particularly for combustion of streams rich in hydrogen. Any nitrogen present in the PSA tail gas would also need to be considered, as fuel NOx would then still be formed, and this route may not be effective. Also the impacts of increasing the size of the ASU to supply additional oxygen would need to be considered.

5.12. Oxygen production

Oxygen purity should be optimised, considering both the impact on the specific power required for oxygen production and the impact on the requirements for removal of argon / nitrogen in purification of the product hydrogen. High purity (99.5 mol%) oxygen is typically achievable economically in large scale cryogenic air separation, the balance then being argon.

Co-production of nitrogen and argon should be considered where there is local demand, where this reduces overall energy requirements. Nitrogen may also be required routinely on site (for example, for blanketing following a trip, continuous purging, or purging following maintenance).

Energy consumption in the ASU should be optimised through flowsheet selection and efficient machinery selection. It is typical for oxygen to be pumped to the required delivery pressure, avoiding an oxygen compressor, with air being compressed and fed to the unit at multiple pressure levels. The ASU and associated air compressor design should be optimised around the oxygen purity and supply pressure requirements of the hydrogen production process.

Heat requirements for regeneration of adsorbers used for drying and purification of compressed air should be optimised, including the best technique for chilling the air to condense and separate water upstream.

Opportunities for recovery and use of heat from the air compression system should be considered if this can be matched with demand within the process, and if this is practical from a technical and commercial perspective, given that the oxygen may typically be supplied from a stand-alone plant by a third party.

The form of heat integration should be selected to avoid additional hazards (for example, through combining oxygen production and hydrocarbon streams). Operability considerations, such as start-up and cool down of the ASU while the hydrogen plant is not operating, would need to be taken into account.

Reduction of the number of compressor cooling stages to increase the compressor discharge temperature and grade of heat available is an option but will also impact compressor selection and increase compressor driver power requirements.

High availability of oxygen supply should be targeted, for example by having parallel equipment or a back-up supply, recognising that interruption of oxygen supply will impact the hydrogen production process, with any commercial and environmental consequences associated with restart following shutdown, such as venting or flaring. The capacity of liquid oxygen production, storage and vaporisation should be optimised to provide back-up to gaseous oxygen production accordingly.

Heat available from air compression in oxygen production

The air compression train in the ASU would typically incorporate large integrally geared compressors, with multiple stages and regular intercooling. In this design, the temperature is kept relatively low (less than 120°C). Unlike in the oxyfuel applications considered previously, there is a requirement to deliver oxygen at high pressure (above feed gas pressure) to the reactor, and there is a need for the air / cycle compressors to operate with a greater number of stages to achieve the delivery pressure.

To recover heat at a higher grade / temperature would require reduced intercooling. In this case heat could be recovered at higher temperature, and there would be more heat available. More power would be required to drive the air compressors due to increased volumes, and a different compressor design or technology would be required. Given the large number of ASUs in service, the compression equipment used is well established.

In the Shell POX (SBHP) process, for example, there would not be an identified use for the low- grade heat, as such heat is also available from the hydrogen production process. The heat could potentially be used in an organic rankine cycle to generate power, and it is expected this would generate less than 0.1 MW per MW of heat available at the lower grade level. It would be higher if the number of intercooling stages was reduced, although this increase would likely be more than negated by increase in the air compression power. With air compression for a 500 tonne/day Shell Blue Hydrogen Facility requiring around 30 MW of power, and requiring a similar amount of cooling, addition of an organic rankine cycle could potentially produce 2 MW of power. This could be assessed using cost-benefit analysis and would also need to take account of any implications for safety reliability and operability, for example.

In this example, 6% recoverable heat from the ASU compression system with an organic rankine cycle could be achievable and this could be higher with direct heat integration.

5.13. Water treatment for re-use

Water / steam is both consumed in the hydrogen production process and used as a medium for recovery and transfer of heat. Water is therefore condensed both from the steam being used as a utility and from cooling of streams within the process.

By-products of the hydrogen production process, such as methanol and ammonia, which are expected to be present in condensed water from the process should be identified and quantified.

A large proportion of water condensed in the process can be re-used, but there is a need to release some water to effluent to avoid build-up of dissolved solids or other impurities.

For condensed water that is to be reused following treatment, any processing requirements for contaminant removal to allow reuse need to be identified, and any effluents and emissions from the proposed processes defined.

Requirements to remove dissolved gases, including CO_2, from the boiler feed water to reduce corrosion should be identified together with associated emissions to atmosphere associated with this deaeration.

For condensed water directed to effluent, impurities need to be identified to allow an appropriate strategy to effluent treatment to be developed, together with any other effluents from within the facilities.

All waste water streams are to be identified, including process condensate and other effluents such as steam system blowdown, cooling water blowdown, rain water, oily water, water treatment effluent and water used for cleaning. Suitable segregation strategies and methods of treatment to meet discharge consent limits are to be defined.

Water consumption and volume of contaminated water should be minimised by through design of the hydrogen production process, optimisation of water management through segregation of contaminated water streams (from water wash, condensate) and of non-contaminated water streams (once through cooling, rain water).

Water treatment should follow the most apt source of emissions limits on a case by case basis, between the existing BAT conclusions for common waste water and waste gas treatment / management systems in the chemical sector (2016/902/EU) and BAT conclusions for the refining of mineral oil and gas (2014/738/EU) and the associated BRef.

5.14. Reliability and availability

Environmental impacts of equipment or systems being unavailable should be identified, with the need for redundancy, buffer storage, etc. considered, to reduce the frequency of the occurrence of other than normal operating conditions (OTNOC). A risk-based OTNOC management plan should be implemented which identifies potential scenarios, mitigation measures (for example, around design and maintenance of equipment critical to avoiding emissions), monitoring and periodic assessment.

Such impacts within the facility could include for example:

- disruption to operation, with flaring required on shutdown and subsequent start-up
- requirement for venting of captured CO_2, for example when downstream CO_2 compression, CO_2 conditioning or export route is not available. It should be an objective of the design to minimise flow / duration of CO_2 venting under such circumstances to maximise overall CO_2 capture rates
- requirement for short term turndown of hydrogen production and flaring of hydrogen if the downstream export route or demand is lower than minimum feasible hydrogen production rate
- loss of performance of emissions abatement systems

Target availability for systems critical to environmental performance should be established, with proposed configuration supported by reliability, availability, and maintainability assessments.

5.15. Flexible operation

Until sufficient hydrogen supply, hydrogen demand or hydrogen networks and storage capacity are established, hydrogen production plants may be required to provide flexible operation to balance variation in demand by hydrogen users.

It is expected that all hydrogen production plants will provide a level of flexibility, at least for example in terms of production capacity range.

The need for high levels of flexibility will affect design and operation, with impacts such as:

- a greater need for intermittent CO_2 venting and feed gas or hydrogen flaring
- greater periods of non-steady state operation with ramp-up and ramp-down of capacity
- a need for wider capacity turndown range
- more regular shutdown and start-up operations
- lower energy efficiency, with potential need for process simplification and reduced heat integration to improve operability
- reduced energy efficiency when operating at turndown or in non-steady state operation
- additional energy requirements for start-up
- reduced CO_2 capture rates, particularly for non-steady state operation
- increased emissions to atmosphere from combustion equipment when operating at turndown or non-steady state operation

Applicants should identify performance at steady-state across the proposed production capacity range from minimum turndown to maximum production.

Flexible operating scenarios, including ‘off-design’ scenarios, where environmental performance will be reduced, or where additional emissions are expected, should also be identified, with examples including:

- rapid changes in capacity
- demand for hydrogen below minimum turndown production capacity with the need for hydrogen to be temporarily flared
- start-up following enforced shutdown

Considering the plant flexibility requirements and associated operating scenarios, the measures taken to maximise environmental performance should be described by the applicant, including for example process and equipment design, selected equipment capacities, and process control strategies.

On the expectation that the flexibility needed from hydrogen production plants may reduce over time, the applicant should also demonstrate a strategy for maximising performance when such flexibility is not required.

5.16. Monitoring and measurement

5.16.1. Role of monitoring

A key requirement of monitoring of the hydrogen production / CO_2 capture process is to demonstrate that the emissions from the process are not causing harm to the environment. Monitoring is also required to demonstrate that resources such as feed gas, electricity and water are being used efficiently, that the CO_2 capture rate is as expected, and that the hydrogen and CO_2 products meet the necessary specifications for export.

Monitoring plans shall be included in the permit application for routine operation and for more extensive monitoring during the commissioning period. During the commissioning period, the operating envelope of the process will be established. Operation at this time may be outside the normal operating envelope, and it is important that the monitoring plan considers any risks, such as to air quality. On completion of commissioning, with operation within the established normal operating envelope, the monitoring plan for routine operation should be implemented.

In addition, for post combustion capture, the operator must demonstrate that the process is being managed to prevent (or minimise) the formation of degradation products, and that where they are formed (and may be released) they, and any capture solvent emissions, are abated to the appropriate level.

5.16.2. Monitoring emissions to air

Monitoring of emissions to air, will be required based on expected pollutants (for example, ammonia, amine compounds, SO_2, NO_x, carbon monoxide, and so on) with appropriate methods and measuring techniques employed.

Monitoring shall consider, for example:

- NO_x and carbon monoxide emissions from combustion
- SO_2 emissions from combustion where the fuel source contains sulphur
- ammonia emissions where SCR / SNCR is employed
- amine / amine degradation products and other volatile solvent emissions
- methane
- hydrogen [Ref. 26,27]

For combustion plant, monitoring is required to demonstrate compliance with the applicable emissions limits described in section 5.11.

The regulators will take a case by case decision on the monitoring requirements, based on the most apt monitoring principles and monitoring thresholds set out for individual pollutants in the BAT Conclusions for Refining of Mineral Oil and Gas or BAT Conclusions for Large Combustion Plant.

Where emerging techniques are used for hydrogen production with CO_2 capture, monitoring methods and standards may need to be developed. Proposals should be developed by the operator as part of the permitting activities.

Where post-combustion CO_2 capture is employed, for example using amine solvent, monitoring of relevant emissions of such as ammonia, volatile components of the capture solvent and likely degradation products such as nitrosamines and nitramines shall be included. Monitoring of specific pollutants arising from post-combustion capture may be by CEMs if available or periodic extractive sampling and where aerosol formation is expected must be isokinetic.

5.16.3. Monitoring emissions to water

Monitoring of emissions to water, will be required based on expected impurities (for example, ammonia, amine compounds, methanol, CO_2, and so on) with appropriate methods and measuring techniques employed.

Monitoring standards for discharges to water should follow the existing BAT conclusions for Common Waste Water and Waste Gas Treatment / Management System in the Chemical Sector (2016/902/EU).

5.16.4. Monitoring of CO_2 capture performance

Applicants should clearly identify how the CO_2 capture performance of the plant will be monitored.

CO_2 capture performance is expected to be monitored according to standards that are recognised under the UK ETS. Measurements required to monitor CO_2 emissions to atmosphere may, for example, include direct measurement of the flow and composition of fuel gas to combustion systems.

This, together with measurement of the flow and composition of feed gas, hydrogen product (including methane content where applicable) and CO_2 product streams, will allow monitoring of the CO_2 capture rate and CO_2 quality (considering any impurities that could impact downstream systems).

5.16.5. Monitoring of process performance

Key requirements for monitoring of process operations should be identified where these ultimately impact on environmental performance – including for example amine system performance, including monitoring of amine solvent quality such as amine concentration, pH and presence of degradation or corrosion products; amine temperatures; amine and wash water circulation rates; rich and lean amine CO_2 loading; and stripper reboiler steam rates.

Energy efficiency in the hydrogen production and CO_2 capture processes should be monitored through measurement of feed and product gas flows and electrical power consumption to calculate overall energy consumption.

Requirements for process performance monitoring, either online or offline, will also be a condition of the permit.

5.17. Flaring

Strategies to reduce flaring and associated emissions should be established, including:

- flaring rather than venting, where emissions cannot be eliminated and where practicable, to minimise emissions of higher global warming potential gases such as methane and hydrogen
- plant design to maximise equipment availability and reliability (per section 5.13)
- minimising emissions under start-up, shutdown, and abnormal operations. Means of achieving this include:
    - use of a flare gas recovery system with adequate capacity
    - routing gas that would be flared to alternative users
    - use of high integrity relief valves
    - other measures to limit flaring to other than normal operations
- managing production of off-gas and balance against requirements for fuel gas using advanced process control and so on
- special procedures to define operations including start-up and shutdown, maintenance work and cleaning

- robust commissioning and handover procedures to ensure that the plant is installed in line with the design requirements
- robust return-to-service procedures to ensure that the plant is recommissioned and handed over in line with the operational requirements
- flaring devices design to enable smokeless and reliable operations and to ensure an efficient combustion of excess gases when flaring under other than normal operations
- monitoring and reporting of gas sent to flaring and associated parameters of combustion

5.18. Venting and purging

The applicant should identify venting and purging requirements in each of the processes employed, noting whether either continuous or intermittent, and identifying pollutants expected to be present, including for example CO_2, carbon monoxide, methane, hydrogen, ammonia vapour or methanol vapour.

Requirements for continuous venting may include for example:

- water vapour from CO_2 dehydration systems using circulating tri-ethylene glycol
- deaeration of steam condensate / boiler feed waters
- gases from processing of waste water streams
- purge of tanks, vent or flare headers

Requirements for intermittent venting may include for example:

- CO_2 vented in abnormal conditions, such as when the downstream transportation and storage system is not available, or if the CO_2 does not meet the export specification
- venting needed as part of purging equipment as part of maintenance activities

For each emissions point, an environmental risk assessment shall be made, against the applicable Environmental Assessment Level (EAL), in accordance with the relevant Regulator’s standard methodologies. This should include justification for venting to atmosphere vs. routing to flare and identification any measures proposed to reduce emissions of pollutants or ensure adequate dispersion. Methane and hydrogen greenhouse gas emissions shall be eliminated as far as practicable.

5.19. Unplanned emissions to the environment

5.19.1. Loss of containment

Consideration should be given to the environmental hazards posed by possible accidents and their associated risks specific to the hazards of the materials used, the operation and maintenance of the plant and the processes involved. This should include the practicality of measures to reduce risks and hazards and to respond to any accidents. In comparing the effectiveness of techniques to prevent emissions, consideration should not be limited to looking at normal operations, but also at the possibility of unintentional releases.

In considering the composition of the fluids that could be released, potential for changes due to degradation during operation should be considered.

Strategies to the reduce the potential for loss of containment and minimise environmental impacts should be established, for example:

- use of special procedures and/or temporary equipment to maintain performance when necessary to manage special circumstances such as spills, leaks, and so on
- use of a risk based leak detection and repair programme where applicable in order to identify leaking components and to repair these leaks
- plant design to facilitate monitoring and maintenance activities by ensuring accessibility
- selection of high integrity equipment where available
- plant design to maximise inherent process containment features

5.19.2. Leak detection and repair

A leak detection and repair programme should be proposed, using industry best practice to manage releases from joints, flanges, seals and glands, and so on. The proposals shall be appropriate to the capture solvents and other fluids used in the process.

5.20. Noise

BAT is to be implemented for prevention or reduction of noise, with a plan for management of noise developed as appropriate to the local environment.

Noise reduction techniques to be considered where necessary to include use of acoustic insulation or enclosures or screening through use of embankments or walls.

Equipment generating noise should be identified at the design stage, and their environmental performance should be considered for intended operations, including:

- an environmental noise assessment
- a noise management plan
- plant design to consider the selection of enclosures of noisy equipment or operations
- plant design to consider the location of noisy equipment or operations
- plant design to consider the use of embankments to screen the source of noise
- plant design to consider the use of noise protection walls

6. Process performance parameters

The performance parameters summarised below are indicative of a range of typical technologies for hydrogen production with CO_2 capture.

These are provided for information, and to highlight key differences between alternative production technologies, and not as an expectation of minimum performance or exhaustive in terms of technology options.

Permit applicants / operators should provide these key performance parameters based on design expectations at the application stage. Subsequent reporting of performance during operation will allow data gathering and enable benchmarks to be established.

Data is provided for:

- GHR + ATR – Low Carbon Hydrogen (LCH^{TM})[13] Process

Based on information provided by Johnson Matthey, with wider considerations from Progressive Energy.

This assessment is based on a feedstock with 89 mol% methane, 7 mol% ethane, 1 mol% propane, 0.1 mol% butanes, 2 mol% CO_2 and 0.9 mol% nitrogen. Hydrogen purification is via pressure swing adsorption to meet purity close to 100 mol% with the off-gas stream used to fuel an auxiliary heater and boiler. CO_2 capture from the process upstream of hydrogen purification, uses activated MDEA solvent. There is a requirement for the import of electrical power.

- POX (Non-Catalytic) – Shell Blue Hydrogen Process (SBHP)

Based on information provided by Shell Catalysts & Technologies.

This assessment is based on feedstock with 91 mol% methane, 5 mol% ethane, 2 mol% propane, 1 mol% CO_2 and 1 mol% nitrogen. Hydrogen purification is via methanation to meet purity > 98 mol% and avoiding production of an off-gas stream. CO_2 capture from the process

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[13] LCH is a trademark of the Johnson Matthey Group of Companies

upstream of hydrogen purification, using proprietary ADIP-Ultra[14] amine solvent. This provides near 100% capture of carbon present as CO_2 in the process stream. With no atmospheric combustion of fuel required, there are no significant direct CO_2 emissions associated with hydrogen production. There is a requirement to import electrical power. Some carbon, in form of methane, remains in the hydrogen product following methanation, which will lead to a CO_2 emission by the end user. The contribution of methane slip with the product hydrogen is excluded in assessing heating value for energy conversion.

Note – a pressure swing adsorption (PSA) unit could be used in place of methanation, to produce a hydrogen purity close to 100 mol%. This would lead to a tail gas for which a beneficial use / disposal route would need to be identified.

- SMR + Post-combustion Capture (PCC)

Based on information from “Benchmarking State-of the Art and Next Generation Technologies”, prepared for BEIS by Wood [Ref. 20].

This assessment is based on feedstock with 89 mol% methane, 7 mol% ethane, 1 mol% propane, 0.1 mol% butanes, 2 mol% CO_2 and 0.9 mol% nitrogen. Hydrogen purification is via pressure swing adsorption to meet purity close to 100 mol%, with the off-gas stream used together with feed gas to fuel the reformer furnace. CO_2 capture is from reformer furnace flue gas only, with 90% CO_2 capture rate using proprietary amine solvent. Power requirements are in this case balanced with self-generation from high pressure steam from the heat recovery system.

The 90% CO_2 capture rate in this case is representative, although it is expected that a design post-combustion CO_2 capture rate of 95% will in most cases be feasible both technically and economically [Ref. 6, 21]. Justification shall be provided by applicants if a design CO_2 capture rate less than 95% is proposed.

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[14] ADIP is a technology licensed by Shell

6.1. Process / energy efficiency

Table 20: Process / energy efficiency key performance parameters

Parameter	Description	Value GHR+ ATR+ PSA	Value POX+ Methanation	Value SMR+ PCC+ PSA	Units
Gross feed gas energy conversion	Energy content hydrogen product / energy content feed gas (LHV basis)	80.6	76.6 + 3.1 (Note 1)	67	%
Net feed gas energy conversion **(Note 2)**	Energy content of net hydrogen product / energy content feed gas (LHV basis)	70.5	70.5 + 3.1 (Note 1)	67	%
Electrical power consumption (Note 3)	Net power import after electrical power generation	8.8	5.6	0	MJ / kg H_2
Overall energy conversion	Energy content hydrogen product (LHV basis) / overall energy input (LHV basis & including power import)	76.1	73.2 + 3.0 (Note 1)	67	%
Water consumption (process)		3.8 (Note 4)	2.4 (Note 4)	5.3 (Note 4)	kg H_2O / kg gross H_2
Auxiliary heating duty	Thermal input if not covered in the above	(Note 5)	(Note 5)	(Note 5)	MJ/ kg H_2

Cooling duty	Heat rejected to cooling medium or air	(Note 6)	(Note 6)	(Note 6)	MJ/ kg H_2

The performance parameters included have each been developed on a different basis, and do not provide a fully like-for-like comparison.

Notes:

1) In the values shown for POX with methanation, 3.1% of feed gas energy retained in hydrogen product in the form of methane – i.e. converted from carbon monoxide/CO_2 as part of the purification step. This avoids use of pressure swing adsorption, with the loss of around hydrogen product in the associated tail gas stream, for which there is no requirement for use as fuel in the process.
2) The Net Hydrogen Product is equal to the Gross Hydrogen Product minus the amount of hydrogen that would be required to generate the imported electricity. This is assumed in the values shown here to be generated using a Combined Cycle Gas Turbine fueled by hydrogen with a 58.5% LHV overall efficiency (based on the top of range of the BAT-associated energy efficiency level for combined cycle gas turbines in the range 50-600 MWth from Table 23 of the Large Combustion Plant BAT conclusions, 2017. BAT Conclusions for large combustion plant
3) The electrical power consumption in each case is on a broadly comparable basis, although with some differences in assumptions, for example around CO_2 delivery pressure.
4) Water consumption is made up of water used in reaction to produce hydrogen and CO_2 plus any condensed water from the process that is not re-used and blowdown from the steam and cooling systems. The data provided by technology is unlikely to be on a fully comparable basis. Operators will need to justify their water consumption on site-by-site basis.
5) All heating duties are included in the feed gas energy conversion figures.
6) Duties include hydrogen rich product cooling, amine cooling in the CO_2 capture unit, flue gas cooling for post-combustion capture, and compressor cooling for CO_2 and air compression. The data provided by technology is unlikely to be on a fully comparable basis. Operators will need to justify their choice of cooling technique(s) and water use on site-by-site basis

6.2. Emissions

Table 21 – Emissions key performance parameters*

Parameter	Description	Value GHR+ ATR+ PSA	Value POX+ Methanation	Value SMR+ PCC+ PSA	Units
CO_2 emissions to air (from the installation)	CO_2 not captured or part of hydrogen product	0.3-0.4 (0.34 - 0.46) (Note 1)	0.0 (0.36) (Note 2)	1.0 (Note 3) 0.5 (Note 4)	kg CO_2/ kg Gross H_2 (kg CO_2 / kg Net H_2)
NO_x emissions to air*					kg / kg H_2
SO_2 emissions to air*					kg / kg H_2
CO emissions to air*					kg / kg H_2
Emissions to water – methanol*	To effluent treatment.				kg / kg H_2
Emissions to water – ammonia*	To effluent treatment.				kg / kg H_2

Parameter	Description	Value GHR+ ATR+ PSA	Value POX+ Methanation	Value SMR+ PCC+ PSA	Units
Emissions to water – CO_2*	To effluent treatment.				kg / kg H_2
Waste production*	For waste stream. Expressed over lifecycle, annually or per unit of hydrogen produced, as appropriate.				kg

The performance parameters included have each been developed on a different basis, and do not provide a fully like-for-like comparison.

*: Data which has not been provided here will be reported and verified during the operational phase of relevant installations. Emissions will be required to comply with all ELVs required under the relevant BAT conclusions.

Notes:

1) Based on ~100% CO_2 capture upstream of the PSA unit, with combustion of the remaining carbon monoxide and methane in the tail gas from the PSA unit to fire auxiliary heater and boiler without further abatement.
2) Based on ~100% CO_2 capture including methanation unit producing 98 mol% hydrogen product. The hydrogen product when combusted offsite will produce approximately 0.33 kg CO_2 per kg H2 product.
3) Based on 90% CO_2 post-combustion capture from reformer furnace flue gas.
4) Based on the expected 95% CO_2 post-combustion capture from reformer furnace flue gas.

6.3. Carbon capture performance

Table 22: Carbon capture key performance parameters

Parameter	Description	Value GHR+ ATR+ PSA	Value POX+ Methanation	Value SMR+ PCC+ PSA	Units
Gross basis					
CO_2 Capture	From Process (Pre-Combustion)	8.4	8.4	0	kg CO2 / kg gross H_2
CO_2 Capture	Post-Combustion	0	0	9.2/9.7 (Note 1)	kg CO2 / kg gross H_2
Total CO_2 Capture	Overall Pre- and Post-Combustion	8.4	8.4	9.2/9.7 (Note 1)	kg CO2 / kg gross H_2
Net basis					
CO_2 Capture	From Process (Pre-Combustion)	9.6	9.1	0	kg CO_2 / kg Net H_2
CO_2 Capture	Post-Combustion	0	0	9.2/9.7 (Note 1)	kg CO_2 / kg Net H_2
Total CO_2 Capture	Overall Pre- and Post-Combustion	9.6	9.1	9.2/9.7 (Note 1)	kg CO_2 / kg Net H_2

Parameter	Description	Value GHR+ ATR+ PSA	Value POX+ Methanation	Value SMR+ PCC+ PSA	Units
Total CO_2 Capture Efficiency	Carbon Captured / Carbon in Feed Gas	95-97	96-97 (Note 2)	90/95	% kg carbon captured / kg carbon in feed gas
Total CO_2 Capture Heat requirement	Net Heat Input to CO_2 Capture Process	Note 3	Note 3	Note 3	MJ / kg CO_2
Total CO_2 Capture Power requirement	Net Power Input to CO_2 Capture Process	Note 4	Note 4	Note 4	MJ / kg CO_2 captured
CO_2 Compression Duty requirement	For Delivery to Pipeline	Note 4	Note 4	Note 4	MJ / kg CO_2 captured

The performance parameters included have each been developed on a different basis, and do not provide a fully like-for-like comparison.

Notes:

1) Lower value based on 90% CO_2 capture, higher value based on 95% CO_2 capture.
2) Based on ~100% CO_2 capture upstream of a methanation unit producing 98 mol% hydrogen product. The hydrogen product will contain 3 to 4% of the carbon from the feed gas. There are no direct CO_2 emissions from the hydrogen production or methanation units.
3) This is included in the feed gas energy conversion rates in Table 20.
4) Included in the power requirements in Table 20.

7. Summary of stakeholder input

This guidance document includes inputs from engagement with key stakeholders, including hydrogen production and carbon capture technology providers, hydrogen project developers and operators.

A questionnaire has been compiled to address the most relevant environmental aspects specific to hydrogen production from methane and CO_2 capture technologies (Appendix A).

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Appendices

Appendix A – Stakeholder engagement questionnaire

Requested information

Stakeholders are requested to provide any information they consider to be of value in assessing BAT for hydrogen production with CO_2 capture, and in particular information addressing the questions below.

If there is information available to stakeholders which is commercially sensitive / confidential and cannot be shared for the purposes of this research, please advise.

The points below consider hydrogen production through forms of autothermal reforming or partial oxidation. In the case of steam methane reforming, some questions will not be applicable, but we are interested also to understand technology and proposals for post-combustion CO_2 capture and atmospheric emissions from the reformer, overall energy balance and utilisation of excess steam.

A. Overall material balance

1. What is the typical hydrogen production capacity range considered, per process train?
2. What are the considerations in scaling the technology to higher capacity or for smaller scale hydrogen production?
3. Would it be possible to share block flow diagrams or simplified process flow diagrams? If so, could these be disclosed in the research report?
4. What is the consumption of feed gas (converted to hydrogen, $CO_{2,}$ and fuel streams) and water per unit of hydrogen production? How much oxygen is generated to supply the process?
5. How is the methane conversion to CO and CO_2 in the reforming section balanced with requirements for CO shift – i.e., degree of conversion?
6. What technologies are proposed for CO shift, for optimal conversion to CO_2, balanced against CO removal duty in downstream hydrogen purification?
7. What level of sulphur contaminants can typically be allowed in the feed gas, what technologies are used for sulphur removal, and in what form is the sulphur captured and disposed of?
8. In the specific case of non-catalytic partial oxidation, how is it proposed sulphur is managed to meet product specifications in terms of upstream or downstream removal?

9. What is the proposed purity of oxygen supply, representing the balance between the need to remove inert components from the hydrogen product and the associated energy requirements for oxygen production?
10. Have applications been identified where methanation could be an appropriate alternative to pressure swing adsorption to meet the hydrogen product specification?
11. How is it proposed to utilise:
    a) Tail gas from hydrogen purification, which depending on the upstream process performance will contain carbon as CO_2, CO, and methane?
    b) Flash gas from CO_2 capture?
12. How is it proposed condensed water from the process is reused and what are effluent streams from process, steam, and cooling systems?

B. CO_2 capture

1. What technologies are proposed for CO_2 capture from the hydrogen rich product?
2. How can the CO_2 capture system be designed to reduce energy requirements – for example, use of split stream absorption, heat integration, flash, etc. in the case of chemical absorption processes.
3. Have other technologies been identified that could reduce energy use or environmental impacts, and what are the obstacles to implementing these?
4. Has the impact of CO_2 capture technology on the CO_2 delivery pressure and downstream CO_2 compression requirements been assessed?
5. Have alternative locations in the process for CO_2 capture been evaluated (to suit technology selection) – for example, removal upstream of hydrogen purification vs. removal in the hydrogen purification unit followed by separation from the purification unit tail gas?
6. Where auxiliary boilers or fired heaters are used, with carbon-containing fuel, has the case for post-combustion carbon capture been assessed?
7. What are the impacts and the implications on emissions to all media under the following operations?
    a) Changes in hydrogen demand
    b) Partial shutdown (for example, of CO_2 export route or hydrogen export route) either planned or unplanned
    c) Interim non-availability of CO_2 transportation and storage infrastructure if timescales for development differ

8. Are there any specific provisions for CO_2 capture readiness in the case of staggered development, i.e., hydrogen production being developed first followed by CO_2 capture at a later stage?
9. Are there any specific provisions for interim operations and associated emissions, prior to the availability of the CO_2 export and storage infrastructure, if this were economically viable?

C. Energy balance

1. How are the overall energy requirements satisfied for hydrogen production and CO_2 capture, including external power and heat requirements and their generation?
2. How are heat exchange and heat recovery systems optimised with the steam system to provide process heating needs including for CO_2 capture?
3. What are the needs for auxiliary boilers or fired heaters, for gas pre-heating or to meet steam balance, and what fuel is proposed for these duties – for example, feed gas, hydrogen rich gas, tail gas from hydrogen purification or hydrogen product?
4. What other potential integration opportunities are there between hydrogen production and CO_2 capture?
5. How is the integration optimised such that the environmental impacts are minimised i.e., energy usage versus operability and any increased emissions during plant upset/non-steady state operation?

D. Process units, scale and experience

1. What process units are proposed for the following?
    a) Sulphur removal
    b) Hydrogen production
    c) CO shift
    d) CO_2 Capture
    e) Hydrogen purification
    f) Oxygen production
    g) Steam and water
    h) Heat and power
2. In which process units is there less operational experience in identical or analogous duty compared with others?
3. What scale have the proposed process units / technologies been used at? What examples are there of plant installations /operations and their associated environmental performance – energy efficiency, minimising continuous/intermittent emissions to air/water/land, waste/water minimisation/recycling/recovery, preventing and minimising consequences of accidents?
4. How has learning from international experience been accounted for?

E. Utilities requirements

1. What are the main utilities requirements for the hydrogen production and CO_2 capture processes?
2. How are utility systems designed and integrated to optimise energy consumption and reduce environmental impacts?
3. Does the hydrogen production process with CO_2 capture require net import or export of electricity? Of Heat?

F. Emissions and waste

1. What continuous or intermittent venting or flaring requirements have been identified? How is this linked with equipment availability and sparing – for example, for CO_2 compression? What availability target is proposed and under what circumstances would hydrogen production continue without CO_2 capture?
2. What are the main solid or liquid waste streams, and how is it proposed these are minimised / recovered / recycled / disposed of?
3. How is process condensate and blow down water segregated, recovered, and reused?
4. What are the main sources of emissions to air and water and how is it proposed these are monitored?
5. Are any chemicals, solvents, catalysts etc. proposed that are potentially harmful to the environment in case of accidental release?
6. What is the fate of any volatile amine degradation products (for example, nitrosamines and nitramines), particularly for any post-combustion CO_2 capture using amines or if captured CO_2 is temporarily vented? Are these limited by water wash on absorber or reflux section above feed in regenerator?

G. Performance metrics

Please provide feedback on the following proposed metrics and any others that are considered relevant to BAT assessment.

1. Process / energy efficiency

Parameter	Description	Units
Feed gas energy conversion	Energy content hydrogen product / energy content feed gas	%
Overall energy conversion	Energy content hydrogen product / overall energy input (including power)	%
Electrical power consumption		MJ / kg H_2
Water consumed by process		kg H_2O / kg H_2
Auxiliary heating duty	Thermal input if not covered in the above	MJ/ kg H_2
Cooling duty	Heat rejected to cooling medium or air	MJ/ kg H_2

2. Emissions

Parameter	Description	Units
CO_2 emissions	Those CO_2 emissions not captured	kg CO_2 / kg H_2
Emissions to air	For component X etc. NOx, CO, etc.	kg X / kg H_2
Emissions to water	For component Y etc.	kg Y / kg H_2
Waste produced	For waste stream. Expressed over lifecycle, annually or per unit of hydrogen produced, as appropriate.	kg

3. Carbon capture performance

Parameter	Description	Units
CO_2 captured from process (pre-combustion)		kg CO_2 / kg H_2
CO_2 captured post-combustion		kg CO_2 / kg H_2
CO_2 captured	Overall pre- and post-combustion	kg CO_2 / kg H_2
CO_2 capture rate	Carbon captured / carbon in feed gas	% kg CO_2 (as carbon) / kg feed gas (as carbon)
CO_2 capture heat duty	Net heat input to CO_2 capture process	MJ / kg CO_2 captured
CO_2 capture power requirement	Net power input to CO_2 capture process	MJ / kg CO_2 captured
CO_2 compression duty	For delivery to pipeline	MJ / kg CO_2 captured

H. Other information

Is there any additional information you propose is considered to support provision of BAT guidance for emerging techniques?