Blue Hydrogen Production Technology Review

Report on behalf of the Bacton Energy Hub
Hydrogen Supply Special Interest Group

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V0.3	20/09/22	Jack Walden	Final Report

EXECUTIVE SUMMARY

This report documents the work of Progressive Energy for the Bacton Energy Hub (BEH) Hydrogen Supply Special Interest Group (SIG). Technologies for the production of hydrogen from natural gas with carbon capture and storage (CCS), along with the auxiliary process stages required, were identified through a literature review to comment on their suitability for deployment as part of the BEH.

The available technologies were then screened by considering several key criteria including maturity, scale of existing installations, and the presence of such technologies in other UK decarbonisation projects. Following screening and shortlisting of the preferred hydrogen production methods, the footprints of major equipment items were estimated to enable the Infrastructure SIG to carry out plot assessments and site safety analyses.

We understand that the Levelised Cost of Hydrogen (LCOH) produced from each process is dependent on more than the core production technology, and is heavily influenced by the technology chosen for auxiliary stages required in the overall process (CO_2 separation etc.). The LCOH from the shortlisted options presented here is subject to variation on a site basis, depending on feedstock quality and product specification. Hence, this report has not considered cost as a criterion for technology selection in this review.

We find that the most suitable technologies for the commercial scale production of hydrogen from natural gas feedstocks in this context are the Gas Heated Reformer + Autothermal Reformer (GHR+ATR), and the Non-Catalytic Partial Oxidation (POX) processes. These technologies are currently either being deployed, or are being considered for deployment, in various industrial clusters around the UK for large-scale, low-cost, low-carbon hydrogen production to facilitate the decarbonisation of heavy industry and domestic gas users. Both technologies provide high thermal efficiency in the conversion of methane to hydrogen, and facilitate the near complete (95%+) capture of CO_2 generated as a by-product for permanent offshore geological storage.

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1.0 ABBREVIATIONS & DEFINITIONS

Abbreviation	Description
ASU	Air Separation Unit
ATR	Autothermal Reformer
BAT	Best Available Techniques
BEH	Bacton Energy Hub
BEIS	The UK Department of Business, Energy and Industrial Strategy
CAPEX	Capital Expenditure
CCS	Carbon Capture and Storage
CCUS	Carbon Capture, Utilisation and Storage
CMS	Carbon Molecular Sieve
DEPG	Dimethyl ethers of polyethylene glycol (a physical solvent for CO_2 separation from gas streams)
GHG	Greenhouse Gas
GHR	Gas Heated Reformer
GTL	Gas to Liquids
HT	High Temperature
IEAGHG	International Energy Agency Greenhouse Gas R&D Programme
I&EC Research	Industrial & Engineering Chemistry Research
LCOH	Levelised Cost of Hydrogen
LT	Low Temperature
MDEA	Methyl-Diethanolamine (a tertiary amine solvent for CO_2 separation from gas streams)

MEA	Monoethanolamine (a primary amine solvent for CO_2 separation from gas streams)
MT	Medium Temperature
OPEX	Operational Expenditure
POX	Partial Oxidation
PSA	Pressure Swing Adsorption
R&D	Research and Development
RFG	Refinery Fuel Gas
SE-SMR	Sorption Enhanced Steam Methane Reforming
SEWGS	Sorption Enhanced Water Gas Shift
Shift	The Water Gas Shift reaction, also termed the CO shift, describes the reversible reaction of water and carbon monoxide to produce hydrogen and carbon dioxide: $H_2O + CO \leftrightarrow H_2 + CO_2$ (-41.2 kJ/mol)
SIG	Special Interest Group
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
tpd	Tonnes Per Day
TSA	Temperature Swing Adsorption
T&S	Transport & Storage (typically referring to CO_2)
UK	The United Kingdom
VSA	Vacuum Swing Adsorption

2.0 SCOPE, APPROACH & OBJECTIVES

This report undertakes to compile and review the current industrially available technologies for the production of Hydrogen (H_2) from Methane[1] (CH_4) with Carbon Capture and Storage (CCS) – so-called 'Blue Hydrogen'. The term 'Blue Hydrogen' is generally avoided in this document to avoid the often-unhelpful stigma arising from its comparison with so-called 'Green Hydrogen' (often used to refer to electrolytically produced H_2). Instead, we prefer the term 'CCS-enabled Hydrogen'. This distinction is important and made based on the principle that electrolytically-produced H_2 relying on electricity from unabated fossil-fuel combustion is likely to be far less 'green' than CCS-enabled H_2 production with high CO_2 capture rates and well-managed, domestically produced methane sources. Therefore, the terms blue and green can incorrectly imply relative environmental credentials and therefore preference of technology, rather than allowing the technology and the specifics of its application to speak for itself.

The technology analysis and review will focus on the core hydrogen production technologies, rather than auxiliary technology packages including but not limited to Air Separation Units (ASUs) or CO_2 Separation packages. This is because these units are either bought commercially 'off-the-shelf' or will be selected on a case-by-case basis by specific projects to account for unique site integration opportunities, CO_2 export requirements or project consortium preferences. Auxiliary equipment will be included in plant footprint and utility requirement considerations, but only a brief overview of their operation will be provided. We also explicitly exclude consideration of the following:

- Upstream gas production, processing, compression and transportation.
- Hydrogen transportation.
- CO_2 transportation and storage beyond the site boundary (taken to be post-compression and conditioning to network/pipeline quality).
- 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.
- Cost (While we acknowledge the importance of cost within project optioneering, this report aims to review the available technologies in terms of their readiness for deployment and environmental performance)

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[1] 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), however these are considered chemically identical to fossil-derived CH_4 sources and hence do not impact the H_2 production technology operation.

The production will be considered for a reference plant of 350 MW_{th} hydrogen production on an HHV basis. The plant is assumed to operate at 95% load constantly, with a 2-week shutdown period in the summer for routine maintenance.

2.1 Key Considerations

Technology assessment 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)
  - Water Consumption
  - Abatement techniques to reduce emissions (e.g. airborne species resultant from solvent degradation)
  - CO_2 capture rate
  - Energy efficiency
  - Hydrogen losses
  - Treatment of captured CO_2 for transport (e.g. quality requirements)
  - CAPEX
  - OPEX
- ➢ 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 (e.g. 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
- Hazardous area
- Plant safety and integrity
- Accident management, leak monitoring and containment arrangements, including loss of containment emissions
- Monitoring for emissions of CO_2

3.0 TECHNOLOGY LONG LIST

3.1 Key Process Steps

Producing hydrogen from methane requires several unit operations, and these vary slightly depending on the core technology being employed. The main process steps for CCS-enabled hydrogen production considered in this report are given below:

- Air Compression/Oxygen Production*
- Feed Gas Pre-Treatment
- Pre-Reforming*
- Reforming/Hydrogen Production
- CO Shift
- CO_2 Capture*
- CO_2 Conditioning & Compression
- Hydrogen Conditioning & Compression

* Indicates that the step is dependent on the production technology selection

For each of these process steps, available and emerging technologies have been identified through a literature review of technical reports in the public domain, including reviews of the Best Available Techniques (BAT) for various industrial processes. These documents include publications from academic institutions, industrial trade associations, and UK and international organisations.

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

- "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 – e.g. for chemical production.
- "Low" is defined as a technology being studied at Research and Development (R&D) level and not yet proven at a pilot scale for manufacturing in the stated industries.

3.2 Air Compression / Oxygen Production

The compression of air is a trivial process in this context, simply requiring a sufficiently sized compressor and an air inlet. Air is required as an oxygen source for hydrogen production by Steam Methane Reforming (SMR) and can be used by Autothermal Reforming (ATR) technologies. ATRs typically make use of pure oxygen due to the thermodynamic and operational benefits it provides.

Oxygen is required as a feed stream in hydrogen production processes using ATR and Partial Oxidation (POX) technologies. The technologies for producing oxygen typically fall into the categories of cryogenic and non-cryogenic air separation, as shown in Table 3-1 below.

Table 3-1: Technology Long List - Oxygen Production

Oxygen Production Technology	Readiness Level	Common Technologies
Cryogenic Air Separation	Mature	Cryogenic Package including TSA and Fractionation
Non-Cryogenic Air Separation	Mature	PSA, VSA, Membranes
Non-Cryogenic Air Separation	Low	Ceramic Membranes

3.2.1 Cryogenic Air Separation

Cryogenic air separation is a mature technology that can produce large volumes 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 liquid oxygen as a product [1]. This liquid oxygen is regasified and used within the process, but can be kept as a liquid for backup supply. ASUs such as this can be sized to produce thousands of tonnes per day (tpd) as required. Designs producing >5,000tpd of oxygen are possible but rarely seen, typically relying on multiple smaller units for resilience.

3.2.2 Non-Cryogenic Air Separation

Non-cryogenic air separation technologies are also mature, but used for lower volume oxygen production and/or lower purity (e.g. between 85% and 95%), not meeting the needs for large scale hydrogen production. The most common non-cryogenic air separation technologies are PSA, VSA and membrane technologies [1]. 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.

3.2.3 Other

Other sources of oxygen, such as the by-product of hydrogen production by water electrolysis could be explored on a site-by-site basis, where there is opportunity for hydrogen production co-location. However, the oxygen would be produced intermittently, at low pressure (and also likely at much smaller scales than would be required by CCS-enabled production technologies) and would require significant compression to be used in an ATR or POX unit.

3.3 Feed Gas Pre-Treatment

Pre-treatment of the feed gas is undertaken to remove any contaminants that might poison sensitive catalysts within the hydrogen production process, or which are dangerous and unnecessary to allow further through the process equipment (such as naturally occurring radioactive material (NORM) from the southern North Sea geology). These impurities are typically sulphur or mercury species, but Refinery Fuel Gas (RFG) streams can also contain chlorides and other heavy metals. Clearly in this case, refinery contaminants are unlikely to pose a significant risk to operation.

The technology required for gas pre-treatment will entirely depend on the feed gas impurities and the catalysts used throughout the process. For example, if a grid-quality natural gas feed is used with a non-catalytic POX unit as the core hydrogen production technology, feed gas polishing may only be necessary to a small degree in order to protect the CO shift catalysts. It is worth noting that hydrogen production at Bacton may have access to high CO_2, non-grid specification natural gas from currently undeveloped fields in the southern North Sea, therefore pre-treatment must be included for consideration.

Examples of technologies which may be employed are given in Table 3-2 below.

Table 3-2: Technology Long List - Feed Gas Pre-Treatment

Contaminant	Readiness Level	Common Technologies
Sulphur	Mature	Catalytic Hydrogenation, Fixed Bed Absorption,
Mercury	Mature	Metal Sulphide bed Absorption
Chlorides	Mature	Fixed Bed Absorption

3.3.1 Sulphur Removal

Treating the feed gas to remove sulphur species is carried out in order to protect the CO Shift and Reforming catalysts from poisoning and subsequent deactivation. Sulphur is removed by a combination of catalytic hydrogenation and adsorption reactions given as Equations 1 and 2 below.

$$RSH + H_2 \leftrightarrow H_2S + RH \tag{1}$$

$$H_2S + ZnO \leftrightarrow ZnS + H_2O \tag{2}$$

The hydrogenation catalyst is typically cobalt-molybdenum based and the H_2S produced is then adsorbed onto a zinc oxide bed. The feed gas is heated to 200 – 400 °C to carry out this process.

3.3.2 Mercury Removal

Treating the feed gas to remove mercury species is carried out in order to protect the Reforming catalysts from poisoning and subsequent deactivation. Mercury would typically be removed via a fixed bed reactor containing a sorbent of sulphur-impregnated activated carbon (denoted as S) or a metal sulphide (MeS). Depending on the selection, the reactions for this step are given as Equations 3 and 4.

$$Hg + S \leftrightarrow HgS \tag{3}$$

$$Hg + 2MeS \leftrightarrow HgS + Me_2S \tag{4}$$

3.3.3 Chloride Removal

Removal of chlorinated species is key for many catalytic industrial processes, as chlorine is another common catalyst poison. Technologies for chloride removal include absorption with Na_2O (caustic) impregnated activated alumina, zinc oxide absorption, or caustic impregnated zeolite absorption [2].

3.4 Feed Gas Pre-Reforming

Pre-Reforming is an optional step used to convert any heavier hydrocarbons present in the feed gas to methane upstream of the main reformer. This is helpful both from a thermodynamic perspective to improve the hydrogen yield (albeit only slightly) and reduce the potential for solid carbon formation and deposition in the reformer, but also from an operational perspective to improve the process resilience to varying feed composition over time. This step is a steam reforming reaction over a nickel-based catalyst which operates at a slightly lower temperature than the main reforming step (c. 450 - 500°C).

In the case of SMR technologies, this stage reduces the required tube area, energy consumption and NO_x emissions due to reduced firing in the main reformer. For ATR-based flowschemes, the pre-reforming step reduces the oxygen requirement and energy consumption.

Several reactions are being carried out simultaneously in this step: two reforming reactions and a small amount of CO Shift. These reactions are given as Equations 5, 6 and 7 below.

$$(CH_2)_n + nH_2O \leftrightarrow nCO + 2nH_2 \tag{5}$$

$$(CH_2)_n + 2nH_2O \leftrightarrow nCO_2 + 3nH_2 \tag{6}$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \tag{7}$$

3.5 Hydrogen Production

The production of hydrogen from methane is the core of the hydrogen production process. Available technologies for this process are given in Table 3-3 below, along with their readiness for deployment for CCS-enabled hydrogen production.

Table 3-3: Technology Long List - Hydrogen Production

Hydrogen Production Technology	Readiness Level	Common Technologies
Steam Methane Reforming (SMR)	Mature	Methanol, Refining, Petrochemical
Autothermal Reforming (ATR)	Mature	Ammonia, Methanol, Gas to Liquids (GTL)
Combined Gas Heated Reforming (GHR) and SMR	Mature	Ammonia, Methanol
Partial Oxidation	Mature	Ammonia, Methanol, GTL
Combined GHR and ATR (Parallel)	Mature	Hydrogen
Combined GHR and ATR (Series)	Mature	Ammonia, Hydrogen, Methanol
Sorption Enhanced SMR (SE-SMR) [3]	Low	Hydrogen
Pyrolysis	Low	Hydrogen
Microwave Technologies	Low	Hydrogen
Dry Reforming	Low	Hydrogen
Plasma Reforming	Low	Hydrogen
Solar SMR	Low	Hydrogen
Tri-Reforming of Methane	Low	Hydrogen

3.5.1 Steam Methane Reforming (SMR)

Steam Methane Reforming is currently the most widely used hydrogen production technology, with an extensive history of large-scale operation in a range of industries. Methane reacts with steam over a nickel catalyst to produce carbon monoxide and hydrogen according to Equation 8. In addition to the reforming reaction, a proportion of the carbon monoxide reacts with available steam according to the water gas shift reaction given again as Equation 7. These can be combined into an 'overall' SMR reaction given in Equation 9.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{8}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{7}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \tag{9}$$

This overall reaction is endothermic, and as such the reforming tubes are heated externally by counter-flowing exhaust gasses from a furnace. The fuel for this heating is typically the tail gas of the hydrogen purification stage of the process, supplemented by natural gas from the feed. Waste heat can be recovered from the flue gas for additional steam raising or other process heating requirements. The outlet of the reformer will contain a significant quantity of unreacted methane and CO due to the high temperatures which do not promote the forward reaction in Equation 7. On a dry basis, a reformer outlet composition of 15 mol% CO and 8 mol% would be typical, however we note that this is a generic composition and reformer exit conditions may vary across industry sectors and flowscheme optimisations. This gas is then cooled and passed to the main CO Shift stage of the process, which will be discussed in Section 3.6.

3.5.2 Autothermal Reforming (ATR)

Autothermal Reforming differs from conventional SMR in that the feed methane is first partially oxidised according to Equation 10.

$$CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2 \tag{10}$$

Combining this with the standard SMR reaction, Equation 8, leads to a combined ATR reaction given as Equation 11.

$$CH_4 + \frac{1}{4}O_2 + \frac{1}{2}H_2O \leftrightarrow CO + \frac{5}{2}H_2 \tag{11}$$

Again, this combined ATR reaction occurs in parallel with the water gas shift reaction given in Equation 7. Combining these into an overall ATR unit reaction gives Equation 12.

$$CH_4 + \frac{1}{4}O_2 + \frac{3}{2}H_2O \leftrightarrow CO_2 + \frac{7}{2}H_2 \tag{12}$$

This configuration enables the ATR unit to operate without an external furnace to provide heat for the endothermic Equation 8, with the heat instead being supplied internally via the exothermic partial oxidation and shift reactions within the process stream. A key advantage of this over conventional SMR is that the resultant CO_2 remains at high pressure within the process stream, facilitating a more attractive opportunity for capturing CO_2 downstream.

3.5.3 Combined GHR and SMR

A Gas Heated Reformer (GHR) makes use of the heat available in the process gas outlet of the SMR to drive the endothermic reforming reactions required to convert heavier hydrocarbons and some of the methane in the feed gas into CO and hydrogen. The GHR comprises a series of catalyst filled vertical tubes, and boasts a more compact footprint and better heat transfer characteristics than the SMR, acting both as a heat exchanger and reactor. Hot syngas exiting the main reformer is fed back into the GHR shell-side to heat the reforming tubes. This facilitates the improvement of the overall energy efficiency of the hydrogen production process compared to a solo SMR flowsheet.

3.5.4 Combined GHR and ATR

The GHR + ATR configuration is more common than the GHR + SMR. This is due to the exothermic nature of the ATR reactions; higher ATR syngas temperatures better serve the purpose of internally supplying the heat for the GHR reactions. These reactors can be arranged either in series (in a figure-of-eight) or in parallel (feed gas is split proportionately between the two reformers to achieve the desired syngas composition).

Arranging the reactors in series facilitates a lower methane slip through the reforming section, and hence a higher CO_2 capture potential for the hydrogen production plant. Lower temperatures in the GHR call for greater steam injection to mitigate against high methane slip.

3.5.5 Partial Oxidation (POX)

Partial Oxidation of methane can be employed to produce hydrogen without any additional reforming reactions taking place. In this case, methane is partially oxidised according to Equation 10, with oxygen typically sourced from a cryogenic ASU. The CO shift reaction, Equation 7, is then used as in previous technologies to increase the hydrogen yield and maximise CO_2 available for capture in the process stream. Heat released from this exothermic reaction is used to generate steam for downstream process use and for more general pre-heating of other processes.

$$CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2 \qquad (10)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (7)$$

As is the case with many industrially mature chemical processes, POX units can be designed as thermal partial oxidation reactors, or catalytic partial oxidation reactors. The main difference between the two is the operating temperature, with catalytic POX requiring significantly lower temperatures at the cost of being vulnerable to poisoning by sulphur species in the feed.

Soot formation and deposition on catalyst beds is a risk associated with feed composition, temperature, pressure, burner design, and flow conditions in the combustion zone [4], resulting in less effective heat transfer and reduction in catalyst performance. This can be controlled and mitigated against by the use of catalysts which ensure the destruction of soot precursors, as well as optimising burner design and flow control solutions. In thermal POX units, soot formation is tolerated in the reactor to a degree determined by downstream equipment, and can be removed by a water wash to prevent carryover into the CO Shift reactors.

3.5.6 Sorption Enhanced Steam Methane Reforming (SE-SMR)

SE-SMR is a novel technology that combines conventional steam-methane reforming with a solid sorbent to capture CO_2 as it is produced and improve the equilibrium conversion of methane to hydrogen. A consortium led by Cranfield University is currently being supported by Phase 2 of the BEIS UK Hydrogen Supply Competition to demonstrate this technology at pilot scale as part of the HyPER Project[2]. This will include the construction and testing of a 1.5 MW_{th} pilot plant at Cranfield University in 2022-23 [3].

Potential benefits of SE-SMR over current commercial-scale production technologies include reduced levelised cost of hydrogen (LCOH) due to the removal of the high energy demand from the solvent CO_2 capture plant, higher capture rates (c.98%), and lower energy requirements [3]. However, these benefits must be demonstrated at scale before significant adoption by industry will occur.

3.5.7 Pyrolysis

Pyrolysis involves the heating of hydrocarbons (in this case, methane) to high temperatures in the absence of oxygen. This produces hydrogen and solid carbon as products, and can also be used to create pyrolysis oils if heavier hydrocarbons are present. The relevant reaction for this application is given as Equation 13.

$$CH_4 \rightarrow C + 2H_2 \qquad (13)$$

Making use of this chemistry for large scale hydrogen production has not been attempted industrially. As such, we consider this an immature technology when used specifically for hydrogen production from methane, while remaining aware that gasification and pyrolysis technologies remain widely used for solid/oil processing.

3.5.8 Microwave Technologies

Microwave reforming technologies aim to reduce the CO_2 emissions associated with conventional methane reforming by electrifying the energy input to the process, rather than relying directly on the combustion of carbonaceous fuels (at least in the case of SMR). In this approach, microwaves are used in conjunction with catalysts to provide the activation energy necessary to carry out the reforming reactions [5]. These technologies do not currently exist at the commercial scales required here.

3.5.9 Dry Reforming

Dry Reforming of methane is also known as CO_2 reforming, because it relies on CO_2 as the oxygen source, rather than steam. This occurs according to Equation 14, typically relying on a nickel-rhodium or ruthenium-based catalyst [6].

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[2] https://www.gov.uk/government/publications/hydrogen-supply-competition/hydrogen-supply-programme-successful-projects-phase-2

$$CO_2 + CH_4 \leftrightarrow 2CO + 2H_2 \tag{14}$$

CO_2 is not currently available as a feedstock in the quantities required; dry reforming makes little sense for consideration here since steam is readily available as a feedstock rather than CO_2, and the objective is to store the CO_2 permanently and remove it from circulation, rather than keep it in the environment.

3.5.10 Plasma Reforming

Plasma Reforming relies on high-temperature (X,000s of °C) plasma to convert methane to hydrogen in both 'dry' (with CO_2) and 'wet' (with H_2O) feed mixtures. These technologies are not available at the commercial scales required in this context and have therefore been discounted for further consideration.

3.5.11 Solar SMR

This technology comprises a conventional SMR process, but where the heat for the endothermic reforming reaction is supplied by concentrated solar power. This is achieved by situating the reactor at the focal point of a parabolic dish, where sunlight is concentrated to produce the high temperatures typically generated by the combustion of fuel gases [7]. This technology is not available at the commercial scale required in this context.

3.5.12 Tri-Reforming of Methane

Tri-Reforming combines the previously described reactions of steam reforming, dry reforming and partial oxidation of methane [8]. The partial oxidation reaction provides some of the heat required by the other two, mitigating the requirement for external heating, similarly to the ATR configuration. This technology is not currently available at the commercial scale required in this context.

3.6 CO Shift

The CO Shift reaction is a catalytic reaction which converts carbon monoxide and water in the syngas exiting the reformer into CO_2 and additional hydrogen, reproduced from Section 3.5.1 as Equation 7.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{7}$$

In order to maximise the hydrogen output and carbon capture potential of the process, a high conversion of CO is desirable. Hence, single-stage Shift configurations are rarely seen. Due to the exothermic nature of the CO Shift forward reaction, heat can be recovered from this step for steam generation, with residual cooling using air or water facilitating the condensation of free water upstream of the CCS package. The catalyst used is dependent on the temperature of the unit and whether the feed is particularly contaminated with sulphur, with optimised bed compositions for high temperature, medium temperature/isothermal, low temperature and sour configurations. Technologies for this reaction, listed with their associated readiness for large-scale deployment in this application, are given in Table 3-4 below.

Table 3-4: Technology Long List - CO Shift

CO Shift Technology	Readiness Level	Relevant Industries
High Temperature (HT) CO Shift **(300 – 450 °C, ≈2.5mol% CO dry at outlet)**	Mature	Ammonia, Hydrogen
Medium Temperature (MT) CO Shift **(220 – 270 °C, ≈0.5mol% CO dry at outlet)**	Mature	Hydrogen
Dual Stage High Temperature/Low Temperature (HT/LT) CO Shift **(LT at 180 – 230 °C, ≈0.2mol% CO dry at outlet)**	Mature	Ammonia, Hydrogen
Isothermal CO Shift **(MT or LT for high conversion of CO. Integrated heat exchange produces steam. Inlet T of 230 °C is typical with outlet P determined by steam production. ≈0.5mol% CO dry at outlet)**	Mature	Ammonia, Hydrogen
Sour CO Shift **(Different catalyst used when the Syngas contains H_2S, outlet contains both H_2S and CO_2)**	Mature	Ammonia, Hydrogen, Methanol
Sorption Enhanced CO Shift **(Combines CO_2 separation into the Shift step through the use of a multi-bed PSA unit)**	Low	Hydrogen

3.6.1 High Temperature Shift

The High Temperature (HT) Shift reactor makes use of the advantageous kinetics of elevated temperatures, at the cost of limiting the equilibrium conversion limit due to the exothermic nature of the forward shift reaction. These reactors typically make use of a copper or chromium promoted iron oxide-based catalyst and operate at temperatures in range 300 – 450 °C. The catalyst is somewhat tolerant to sulphur contamination, with typical practical limits of around 100ppmv, however extended operation with relatively high/variable concentrations will reduce the mechanical strength and limit the catalyst lifetime [9]. Due to the limited equilibrium conversion of CO resulting from the high temperatures, minimum CO concentrations of around 2.5 mol% are typical at the reactor outlet. While this may be acceptable for some applications, when producing hydrogen from methane feedstocks a critical aim is often to maximise the carbon recovery in the captured CO_2 stream for transport and storage. This is achieved through a well-designed CO_2 separation stage of the process, but also by maximising the proportion of input carbon atoms which end up as CO_2 in the product stream. Hence, higher conversions of CO to CO_2 are required here.

3.6.2 Medium Temperature Shift

Medium Temperature (MT) Shift reactors aim to compromise between the advantageous kinetics of elevated temperatures and the higher equilibrium conversion achievable at reduced temperatures. These reactors operate at temperatures in the range 220 – 300 °C and use copper-zinc-aluminium catalysts optimised for the lower temperatures than seen in HT reactors. Typical CO outlet concentrations of 0.5 mol% are expected from MT Shift units.

3.6.3 Dual Stage HT/LT Shift

Installing a Low Temperature (LT) shift reactor downstream of the HT reactor outlet cooling exchanger facilitates more complete conversion of the CO within the process stream. The reactor operates at temperatures in the range 180 – 230 °C, with a copper-zinc-aluminium catalyst. At these conditions, outlet CO concentrations of 0.2 – 0.3 mol% can be expected, however the catalyst is extremely sensitive to poisoning by sulphur. A feed composition of as little as 0.1 ppmv sulphur will lead to catalyst deactivation over time [9].

3.6.4 Sour Shift

Sour shift reactors and catalysts exist for process streams with high sulphur content. These operate with inlet temperatures of around 250 °C, and make use of cobalt-molybdenum catalysts, which require a certain sulphur content to remain in their active sulfided state [9]. These are often configured as several adiabatic beds in series with inter-cooling for temperature control. Outlet CO compositions as low as 0.5 mol% are possible, depending on the number of beds employed, and reactor costs usually result in 2 or 3 beds, reaching CO concentrations of around 0.8 mol%.

3.6.5 Isothermal Shift

The Isothermal Shift configuration is generally achieved by installing several MT shift reactors in series with intercoolers to generate steam and maintain a reasonably constant temperature throughout. In other aspects it will operate the same way as the MT Shift.

3.6.6 Sorption Enhanced Shift

Sorption Enhanced Water Gas Shift (SEWGS) is a novel design which incorporates CO_2 separation by pressure-swing adsorption (PSA) into the shift reactor vessels [10]. Multiple adsorption beds remove CO_2 from the gas stream as it is produced by the forward shift reaction. This technology allows the thermodynamic equilibrium to be shifted to favour the forward shift reaction and achieve near-complete conversion of CO and maximum hydrogen production. The adsorption beds are regenerated by pressure reduction, producing a low-pressure CO_2 stream for compression and introduction to a downstream T&S network. This technology has not been demonstrated at the scale necessary for application here, but opportunities may exist for CCS-enabled hydrogen projects in the coming decade.

3.7 CO_2 Capture

The separation of CO_2 from the hydrogen product is an integral stage of the CCS-enabled hydrogen production process since it facilitates (and is required for) the Transport and Storage (T&S) downstream operation. Removing CO_2 and other acid gases such as H_2S is a mature unit operation that has been developed and optimised extensively over the last 60 years, predominantly for the sweetening of natural gas. In this application, CO_2 can be captured from two major sources:

- Process CO_2 Capture – CO_2 is captured from process streams, most often the hydrogen product stream downstream of the CO shift reactors. This has the main advantages of providing high pressure CO_2 at high concentrations (>20mol%).
- Post-Combustion CO_2 Capture – CO_2 is captured from combustion flue gas streams such as the reformer furnace. These streams are typically at near-atmospheric pressure and contain low concentrations of CO_2 diluted with nitrogen, oxygen and other combustion products.

Technologies available for CO_2 capture are given in Table 3-5 below.

Table 3-5: Technology Long List - CO_2 Capture

CO_2 Capture Technology	Readiness Level [11]	Common Technologies [11]
Chemical Absorption	Mature	Amine solvents and formulations (MEA, MDEA, aMDEA, ADIP ULTRA, UCARSOL®), Hot Potassium Carbonate (Benfield®, Catacarb®)
Physical Absorption	Mature	DEPG (Selexol®, Genosorb®), Methanol (Rectisol®), n-methyl-2-pyrrolidone (Purisol®)
Hybrid Absorption	Mature	Sulfinol®
Cryogenic Separation	Novel at Scale	Low Temperature partial condensation downstream of CO Shift or on PSA tail gas
Membrane Separation	Low	H_2-selective membrane integrated into ATR, Carbon Molecular Sieve (CMS)
Chemical Looping [12]	Low	Metal Oxides
Pressure Swing Adsorption (PSA)	Mature	Adsorber beds with pressure swing regeneration
Vacuum Swing Adsorption (VSA)	Novel at Scale	Adsorber beds with vacuum swing regeneration

3.7.1 Chemical Absorption

Chemical absorption (typically with aqueous amine solutions) relies on the formation of the carbamate ion by reactions with dissolved CO_2. This absorption is exothermic and therefore requires the process gas to be cooled to 60 – 80 °C to promote high CO_2 uptake. Heat recovered from this cooling can be used for steam generation. Pumparound cooling between column trays/packing sections may be employed to maintain acceptable temperatures, but since this is low grade heat there are few options for heat recovery. CO_2 is released in the solvent regenerator (CO_2 stripper) column by the addition of heat in the form of low-pressure steam supply to the reboiler. The reboiler temperature is limited by the thermal degradation temperature of the solvent (typically around 125 °C), and the products are a high purity CO_2 stream for compression, drying and storage, and a high purity hydrogen stream for polishing and export to market.

Chemical solvents are generally susceptible to degradation via exposure to oxygen, SO_X, NO_X and other contaminants, which can cause problems in post-combustion capture applications, but this is unlikely to prove a significant design challenge here due to the lack of the aforementioned impurities in the process gas. Proprietary solvent formulations have been developed by various vendors to improve degradative performance and reduce foaming in the absorber.

3.7.2 Physical Absorption

Physical absorption flowsheets appear very similar to those used for chemical solvents, although typically CO_2 release is governed by pressure reduction in flash vessels, rather than heat addition. Physical solvents are typically better suited for bulk CO_2 removal from process gases with high CO_2 partial pressures and can struggle to reach the high uptakes achievable with chemical solvents. However, high overall CO_2 recoveries are still achievable by appropriately sizing the solvent circulation rate and key equipment.

3.7.3 Hybrid Solvents

Hybrid solvents such as Sulfinol® incorporate the chemical resilience of physical solvents with the high uptake and fast reaction rates of chemical solvents and have applications across the gas processing industry. While these technologies again make use of similar flowsheets to those of chemical and physical absorption, their strengths are in the lower circulation rates required, resulting in smaller equipment sizes and hence lower plant costs. These advantages are often balanced, however, by the higher solvent cost and licensing fees associated with the proprietary technology.

3.7.4 Cryogenic Separation

Cryogenic CO_2 separation technologies are not currently in widespread use at the scale and in the process envisioned here. Major applications are for bulk CO_2 removal or processing in synergy with other activities such as CO_2 shipping, or at least in conjunction with other CO_2 separation technologies such as membranes. Benefits of cryogenic separation are the potential for higher pressure CO_2 delivery, reducing (or removing) the downstream compression requirement associated with solvent absorption processes.

The International Energy Agency Greenhouse Gas R&D Programme (IEAGHG) compared the CO_2 capture rate from SMR-based hydrogen production using MDEA and cryogenic with membrane technology. They conclude that the overall capture rates are comparable, but that the liquefaction and regasification duties of the cryogenic process are likely to be better suited to specific applications outside of large-scale hydrogen production [13].

3.7.5 Membranes

Membrane technologies for CO_2 separation are not currently in operation at the scales required here. They work by providing a selective transport pathway through their structure for specific molecules, while excluding others. Due to their immaturity at scale, they are unlikely to present the most appropriate solution to CO_2 separation in hydrogen production applications.

3.7.6 Chemical Looping

Chemical (or Solid) - Looping operates on the same principle as chemical solvents. CO_2 is passed over a solid (typically CaO) and reacts with it to produce a different solid ($CaCO_3$ in the case of the CaO example). This CO_2-bound solid is then conveyed to another reactor where the CO_2 is driven off into a high-purity stream for compression and storage, regenerating the original solid for re-use [12]. Chemical looping is not currently in use at the scales required for the hydrogen production industry.

3.7.7 PSA

Pressure Swing Adsorption (PSA) is a mature technology which is applied here to separate CO_2 from process gas stream through adsorption onto a fixed bed solid sorbent. The fully loaded beds are then regenerated by reducing the pressure to evolve a low-pressure, high-purity CO_2 stream for compression and storage. This is well suited to polishing applications, where small volumes of CO_2 need to be removed to reach high-purity products, but at the large scale and high throughput of the process required here, other more continuous processes may be more appropriate.

3.7.8 VSA

Vacuum Swing Adsorption (VSA) is a novel technology for carbon capture applications and has been installed at Air Products' Port Arthur SMR based hydrogen production facility [14]. It is the same process that occurs in PSA systems; however, bed regeneration is carried out at sub-atmospheric pressures. This is the first at-scale implementation of this technology in the hydrogen production industry and was selected over conventional amine scrubbing due to the avoidance of the solvent regeneration duty. The high energy costs associated with amine regeneration is a common drawback of chemical solvent systems and VSA appears to provide a viable alternative in the context of an SMR plant. VSA has also been assessed in technology reviews by the Royal Society of Chemistry and Industrial & Engineering Chemistry Research (I&EC Research) [15] [16]. VSA is unlikely to be the technology choice for this application due to its lack of maturity, operational complexity and the need for high-throughput CO_2 removal.

3.8 CO_2 Conditioning

The CO_2 stream arising from the separation stage may be at low-pressure, in a water-saturated state, and may contain impurities that must be removed prior to the downstream T&S network. Since the principal impurity is water, this stage most commonly comprises a compression and drying module, where multi-stage compression to the T&S pressure removes the bulk of the water, and a final ab/adsorption dehydration step is employed to meet the pipeline composition specification.

It may also be necessary to remove oxygen from the CO_2 stream. This is achieved by a catalytic reaction with hydrogen at modest temperatures of around 80 °C, and can therefore be located between the compressor outlet and final drying unit. CO_2 conditioning technologies are given in Table 3-6 below.

Table 3-6: Technology Long List – CO_2 Conditioning

CO_2 Conditioning Technology	Readiness Level	Common Technologies
Physical Absorption (for dehydration)	Mature	Glycol dehydration (MEG, DEG, TEG)
Temperature Swing Adsorption (TSA)	Mature	Molecular Sieve in a fixed bed, regenerated by hot CO_2
Catalytic Oxidation	Mature	Catalytic reaction with hydrogen

3.8.1 Physical Absorption

The process of physical absorption of water is the same as that employed for CO_2 capture described in Section 3.7.2. Solvents for dehydration are typically glycols, which boast high technological maturity and a wide variety of demonstrated applications at scale. However, the presence of glycols in CO_2 T&S systems downstream of the capture plant is limited by the potential to form corrosive liquids, and must be assessed on a system-by-system basis, taking into account parameters such as temperature, pressures, and CO_2 stream impurities.

3.8.2 TSA

Temperature Swing Adsorption (TSA) relies on heading of the adsorption beds to release the adsorbed water. Often called desiccant dryers, this process uses molecular sieves to preferentially adsorb water from the CO_2 stream. Advantages over physical solvents include no carryover of solvent into the CO_2 stream to the T&S network because the sorbent material is solid. This is important in applications where CO_2 pipeline specifications may not allow the presence of glycols due to corrosion concerns, which is a point of critical system importance.

3.8.3 Catalytic Oxidation

Removal of oxygen from the CO_2 stream is key to prevent unwanted oxidative environments downstream in the T&S network or storage site. In the case of CO_2 storage in retired gas fields, microorganisms existing within the rock can use this oxygen to respire aerobically and produce undesirable metabolites, disrupting or altering the project lifespan if at sufficient scale. Oxygen is removed by a catalytic reaction with hydrogen according to the following reaction.

$$O_2 + H_2 \rightarrow H_2O \tag{15}$$

The water produced is then removed by the drying processes described above.

3.9 Hydrogen Conditioning

Once the CO_2 has been separated from the product hydrogen, further conditioning/polishing is needed to whatever degree required by the end use. Hydrogen for fuel cell vehicles, for example, must be provided at 99.999 mol% purity, whereas hydrogen for natural gas fuel switching must meet a grid specification outlined by the regulator[3]. Technologies for hydrogen purification are given in Table 3-7 below.

Table 3-7: Technology Long List - Hydrogen Conditioning

Hydrogen Conditioning Technology	Readiness Level	Common Technologies
Pressure Swing Adsorption (PSA)	Mature	Adsorber beds with pressure swing regeneration
Methanation	Mature	Nickel-based catalysts

3.9.1 PSA

Pressure Swing Adsorption (PSA) is a mature technology which is applied here to separate hydrogen from impurities in the process gas stream through adsorption onto a fixed bed solid sorbent. Hydrogen passes through the beds, and exits the unit at purities as high as 99.999 mol%, while impurities are retained by the sorbent. The fully loaded beds are then regenerated by reducing the pressure to evolve a low-pressure tail gas that typically still contains enough combustible components (including non-recovered

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[3] From a regulatory perspective, as long as the composition of the blended grid gas meets the specification (currently set out in Schedule 3 of the Gas Safety (Management) Regulations, GS(M)R), the composition of the hydrogen being blended in is irrelevant. This clearly requires that the hydrogen not contain any species currently prohibited by the regulator.

hydrogen) to be used a fuel for process heating or steam-raising. The balance between hydrogen product purity and tail gas calorific value is tailored to each site depending on acceptable levels of hydrogen recovery. In general, the higher purity hydrogen required, the lower the overall recovery.

3.9.2 Methanation

Methanation is a catalytic process relying on nickel-based catalysts which converts any remaining CO or CO_2 in the hydrogen to methane according to the following reactions.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{16}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{17}$$

This is a mature technology with extensive history of at-scale deployment in the ammonia and gasification industries. Methanation may be used in conjunction with a PSA unit for so-called ‘five 9s’ hydrogen production (99.999 mol% purity) to facilitate a higher calorific value tail gas, but as long as the methane content does not exceed the hydrogen specification (for lower-purity applications like fuel switching), a PSA is not always required.

4.0 ENVIRONMENTAL CONSIDERATIONS

In reality, the hydrogen production technology ultimately selected for deployment as part of the Bacton Energy Hub (BEH) will be determined by considering a range of technical, economic, commercial and strategic factors. However, it is important that the decision on technology selection and plant configuration also takes into account environmental performance, considering overall energy efficiency, resource utilisation, waste management and CO_2 capture potential.

Electrical power required by the process is also a key factor. The availability of utilities at the site is being assessed by the Infrastructure SIG, hence this analysis will only consider the potential for process requirements, without considering practical site limitations. These will be identified in further work and will inform the wider BEH findings. The source of the required electricity is also important for life-cycle assessments on carbon intensity; however, these details are deemed to be out-of-scope for this report.

4.1 Feed Gas Supply

The hydrocarbon feedstock for the BEH hydrogen production plant could arrive from a variety of sources:

- UK National Grid (NTS) Supply
- Life extended gas fields in the Southern/Central North Sea (where pipelines permit)
- New field developments in the Southern North Sea
- European Gas imports through the Interconnector which makes landfall at the Bacton Terminal

Any CO_2 present in the feed gas will be captured as part of the process, however specific technologies, such as POX units, may operate more optimally with CO_2 content of the feed below 10 mol%. It would likely be preferable to remove nitrogen and other inerts from the feed gas if present at significant concentrations to avoid breaching hydrogen product composition specifications, control NO_X emissions to air and limit the need to oversize equipment and add capital cost to the plant.

A range of feed gas compositions must be considered in plant design, since the source of feed may change (or, in the case of life extended gas fields, composition may shift) over the project lifetime. This is required to specify the Pre-Treatment and Pre-Reforming process stages, with both stages necessary to produce a consistent feed stream to the main reformer unit. SO_X emissions to air are controlled by desulphurising the feed gas, or making use of naturally low-sulphur feed.

4.2 Desulphurisation & 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. Desulphurisation is typically achieved through hydrogenation of sulphur containing compounds and their removal on a catalyst adsorbent. As such, the 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

Pre-reforming transfers duty out of the main reformer, allowing for a reduction in vessel 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, e.g. where it is supplied at grid quality, there may be little or no advantage in pre-reforming.

4.3 Reforming & Shift

Optimising the methane conversion for CO_2 production and H_2 purification are the key environmental factors governing the reforming and shift stages of the process. 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 (referenced earlier in Section 3.5). The need for soot removal, e.g. 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 in order to:

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

A potential strategy to achieve this may be an isothermal shift, with isothermal conditions achieved through reactor cooling with recovery of heat and steam generation. 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 (e.g. 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 [17].

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 also be addressed.

4.4 CO_2 Capture

The UK's recently published Low Carbon Hydrogen Standard provides guidelines for producers to ensure that new-build hydrogen production capacity constitutes 'low-carbon hydrogen' [18]. The standard sets out in detail the methodology for calculating the emissions associated with hydrogen production and the steps producers are expected to take to prove that the hydrogen they produce is compliant. The intent of the standard is to ensure new low carbon hydrogen production supported by government makes a direct contribution to GHG emission reduction targets under the Climate Change Act.

While consideration of the full Scope 1, 2 and 3 emissions of a process will determine its compliance with the Low Carbon Hydrogen Standard, minimising direct (Scope 1) emissions from the process is clearly critical from a permitting and consenting perspective, as well as the main source of emissions directly controlled by the plant design. 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

Technologies which reduce heat requirements for solvent regeneration should be prioritised, such as producing a semi-lean solvent stream for bulk removal in the bottom section of the absorber. These techniques increase overall solvent circulation and pumping requirements but reduce heat requirements for solvent regeneration.

Higher pressure CO_2 recovery options are also preferable, e.g. solvent systems with flash regeneration of a portion of CO_2 at an intermediate pressure, the benefits of which are dependent on the operating pressure of the reforming process and CO_2 absorber. This reduces the compression load in the downstream CO_2 conditioning stage and hence the overall process energy consumption.

Absorber design should minimise carry-over of solvent, e.g. through water wash and/or demisting, to minimise impact on the downstream hydrogen purification process and associated product and off-gas streams. Amine/nitrosamine emissions to air and water are tightly regulated and must be minimised to meet strict environmental constraints.

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.

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.

A design CO_2 capture rate of 95% or greater is expected to be achievable for the hydrogen production plant, noting that the observed capture rate may vary in practice. For ATR with GHR or POX hydrogen production processes, the 95% or higher CO_2 capture rate is dependent on high conversion of 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. Hence, if an overall design CO_2 capture rate of less than 95% is proposed, robust justification should be provided by the applicant.

4.5 Hydrogen Purification

The product hydrogen specification will govern the degree of final purification required to remove impurities entrained in the product stream. It will be necessary to consider:

- Inerts (Nitrogen, Argon etc.)
- Methane (unconverted from the reforming section)
- CO (unconverted from the shift section)
- CO_2 (not captured by the CO_2 capture process)
- Water (saturated from the CO_2 absorber column or unconverted from the shift section)

Where the hydrogen product gas specification allows, and particularly where it is intended that the hydrogen will be blended with methane for downstream distribution, methanation 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.

4.6 Tail Gas

The residual stream from the hydrogen purification process will be rich in hydrogen and will contain the inerts, unconverted methane and CO from upstream processes. This stream is often used as fuel gas to contribute to the heat/steam/electricity demand of the overall process. There is an argument for avoiding high levels of methane or CO slip through the process, as this increases the amount of gas being processed and the hydrogen produced, however the optimum conversion rates may be influenced by the site energy balance and the potential for higher calorific value tail gas to meet energy demands without the need for imports.

In the case of processes with ATR or POX reactions, slip of methane or CO from the reforming and shift stages removed in hydrogen purification will be 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 (due to the exothermic partial oxidation reactions providing heat for steam raising), and tail gas produced from hydrogen purification may not be required to meet the fuel balance. In this case, a use for the tail gas outside of the hydrogen production facility would need to be found, or the hydrogen production facility design adapted to utilise the gas for generation of heat or power, e.g. in superheating of the steam generated in the process. Other technologies with heat liberation in furnaces can be fired with pure hydrogen avoiding the need to combust the PSA purge gas, provided a suitable outlet is available.

4.7 Heat Integration

Optimising heat integration within the hydrogen production process is critical to minimise the amount of external heating and cooling required, and hence the total energy demand of the process. In this process, integration will most likely occur through gas-gas exchange of process streams, steam production and superheating, and through waste heat recovery by water serving to maximise the use of low-grade residual heat.

There is high-grade heat available immediately downstream of the reforming/partial oxidation section, where the process stream is conditioned for the CO Shift reactors. This heat will likely be best used to generate/superheat high-pressure steam for use in the process. Heat recovery from the CO Shift reactors is possible at lower temperatures, but still provides sufficient temperature for low-pressure steam raising for use in CO_2 capture solvent regeneration.

There will almost certainly be additional cooling required against ambient air or cooling water. However, opportunities to maximise heat utilisation should be pursued, such as pre-heating boiler feed or demineralised water.

Where there is the potential for excess steam production from the process, 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.

4.8 Electrical Power

A co-generation unit may be implemented to assist steam and power supply to the hydrogen production/CO_2 capture process and may also enable 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 or other sufficiently high CV streams.

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 [14].

4.9 Water Treatment

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, along with any effluents and emissions from the proposed processes.

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.

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 (cooling, rain water).

Water treatment should follow the most apt source of emissions limits on a case-by-case basis, in accordance the existing BAT Conclusions for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector [18].

4.10 Flaring

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

- Plant design to maximise equipment availability and reliability.
- 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 etc.
- 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.

4.11 Noise

Noise reduction techniques should be considered where necessary and should include use of acoustic insulation or enclosures or screening through use of embankments, walls, or natural barriers such as trees or hedges. It is acknowledged that the proposed site is already occupied by industrial equipment, and therefore some level of artificial noise is likely to be present already. Nevertheless, new noise-generating equipment should be identified at the design stage, and its environmental performance should be considered for intended operations.

5.0 HYDROGEN PRODUCTION TECHNOLOGY SHORT LIST

5.1 Long List Screening

Screening of the technology long list presented in Section 3.5 has been undertaken to produce two options for development in further work. This process has considered:

- Technologies that can achieve the production scale that are likely to be proposed in line with UK decarbonisation objectives and anticipated developments in Bacton
- Technologies with a suitable level of readiness for deployment:
  - Mature technologies applied in equivalent service and at the required scale and design operating envelope (e.g. pressure)
  - Combinations of technologies proven in operation, but not necessarily previously combined in equivalent service or at the required scale
- Technologies that are being considered for current UK projects

5.2 Short List

Having reviewed the available technologies for CCS-enabled hydrogen production, we find that the two most appropriate production technologies for deployment at Bacton are the GHR + ATR and the Partial Oxidation processes. This shortlisting principally relies on the maturity of the technologies themselves, along with their potential for high-CO_2 recovery carbon capture. SMR, while mature, cannot compete on emissions performance with either GHR + ATR or POX.

The following sections will explore and quantify the performance of these processes in order to compare them in more detail.

6.0 HYDROGEN PRODUCTION TECHNOLOGY OVERVIEW

The Technology Long List (Section 3.0) has identified a range of technologies available for the production of hydrogen from a hydrocarbon-rich feed gas. This section will explore the shortlist technologies, GHR + ATR and POX, in more detail and comment on their suitability for deployment at Bacton. Key process performance parameters of these processes (or comparable commercially marketed technology packages) have been compared in wider literature, and this section aims to consolidate these comparisons for use by the Hydrogen Supply SIG [19].

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.

6.1 GHR + ATR

As outlined in Section 3.5.4, the GHR + ATR concept involves passing the feed gas through a GHR reactor to begin reforming a portion of the hydrocarbon content to CO and H_2. The heat required to drive these reactions is supplied by the high temperature outlet stream of the ATR, shown in Figure 6-1. This optimised heat integration facilitates higher thermal efficiency and reduced external heating duty in the process as a whole.

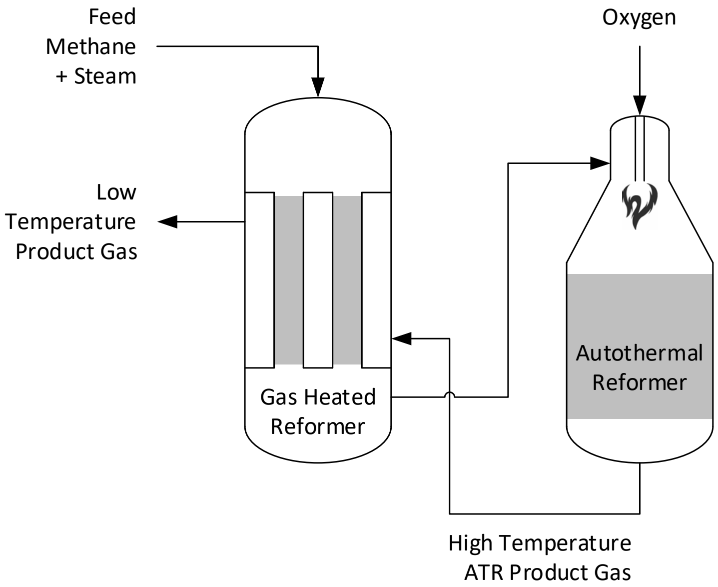

Figure 6-1: The GHR + ATR in series concept.

This assessment is based on the Johnson Matthey (JM) LCH^{TM},[4] process, with a feedstock of 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. The core reforming technology of ATR+GHR can be coupled with other CO_2 removal technologies depending upon project dynamics, resulting in multiple LCH^{TM} technology options. One example of this is $^{8}RH_2$ which combines JM's technology with 8Rivers'[5] proprietary CO_2 removal technology. For simplicity's sake this report has focussed on an amine CO_2 removal system as this is favourable for most projects.

6.2 POX

As outlined in Section 3.5.5, POX units utilise oxygen from an ASU to convert methane to syngas. The heat generated from this exothermic process is used to generate high-pressure steam for use in the CO Shift stage of the process.

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[4] Low Carbon Hydrogen (LCH) is a trademark of the Johnson Matthey Group of Companies

[5] https://matthey.com/en/news/2022/8-rivers#:~:text=As%20members%20of%20the%20Sustainable,Johnson%20Matthey%27s%20industry%2Dleading%20technologies

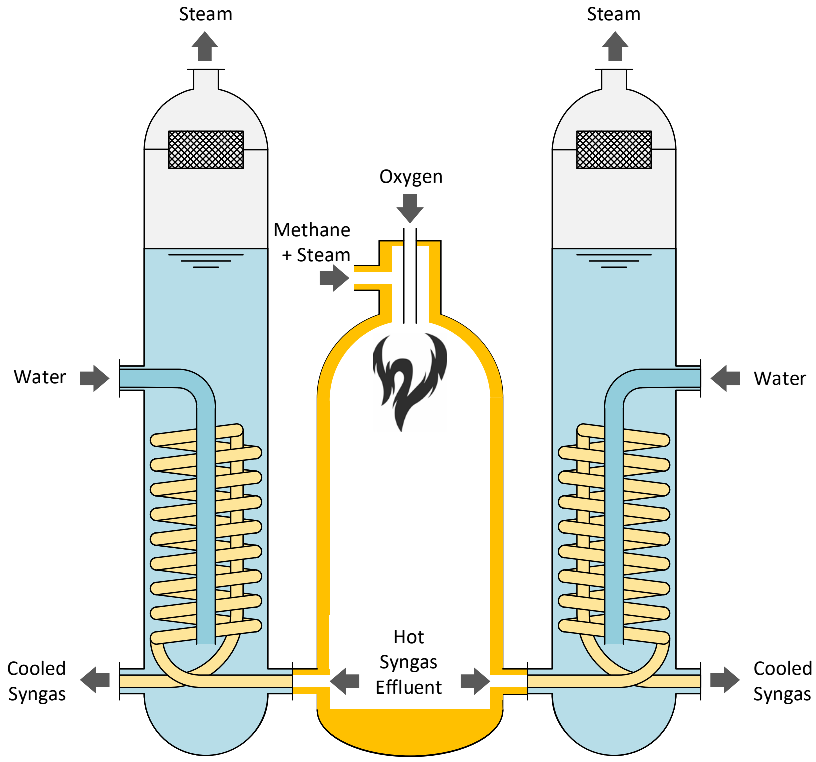

Figure 6-2: Non-Catalytic Partial Oxidation with dual syngas coolers to generate high-pressure steam (Shell)

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 upstream of hydrogen purification, using proprietary ADIP-Ultra[6] 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.

A 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.

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[6] ADIP is a technology licensed by Shell

6.3 Performance Parameters [19]

Parameter	Description	Value GHR+ ATR+ PSA	Value POX+ Methanation	Units
Feed Gas Energy Conversion	Energy Content Hydrogen Product / Energy Content Feed Gas (LHV Basis)	80.6	76.6 + 3.1 (Note 1)	%
Electrical Power Consumption (Note 2)	Net Power Import After Electrical Power Generation	8.8	5.6	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)	%
Water Consumption (Process)		(Note 3)	(Note 3)	kg H_2O / kg H_2
Auxiliary Heating Duty	Thermal input if not covered in the above	(Note 4)	(Note 4)	MJ/ kg H_2
Cooling Duty	Heat rejected to cooling medium or air	(Note 5)	(Note 5)	MJ/ kg H_2
Total CO_2 Capture	Overall Pre- and Post-Combustion	8.4	8.4	kg CO_2 / kg H_2
Total CO_2 Capture Efficiency	Carbon Captured / Carbon in Feed Gas	95-97	96-97 (Note 6)	%, kg carbon captured / kg carbon in feed gas

The performance parameters included have each been developed on a different basis, and do not provide a fully like-for-like comparison. They are reproduced from the BAT for Hydrogen Production from Methane and Refinery Fuel Gas with Carbon Capture [19].

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 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.
3. 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. Although information is available, it is unlikely to be on a comparable basis and has not been included.
4. All heating duties are included in the feed gas energy conversion figures.
5. 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.
6. 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.

7.0 PLANT FOOTPRINT

Understanding the physical size of the plant equipment is key for the Infrastructure SIG to undertake analysis of the available plot and associated safety and layout constraints. A reference plant size of 350 MW_{th} hydrogen (HHV) is anticipated to require the following area for major equipment items [20]:

- ASU: **950** m^2
- Pre-Treatment: **1,000** m^2 (might not be required)
- Reforming/Partial Oxidation: **1,700** m^2
- CO Shift: **2,000** m^2
- CO_2 Capture: **1,800** m^2
- CO_2 Compressors: **250** m^2 (6 MW_e)
- H_2 Purification & Compression: **650** m^2

These estimates are for the equipment footprints only and do not account for the separation distances and boundary margins required by regulations. Configuration of these equipment items on the available site is to be undertaken by the Infrastructure SIG, where these considerations will be quantified and implemented to produce an indicative plot plan.

We note that HyNet has published their Phase 2 Hydrogen Supply Report for BEIS from which a fully developed plot plan for approximately 1 GW_{th} of hydrogen from GHR + ATR requires a plot area of around 20 ha[7].

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[7] https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/1056041/Phase_2_Report_-_Progressive_Energy_-_HyNet_Low_Carbon_Hydrogen__3_.pdf

8.0 CONCLUSIONS & RECOMMENDATIONS

This report presents a technology review for the production of hydrogen from natural gas feedstock, including all major process steps and compression of the hydrogen and CO_2 products to network and storage pressure respectively. We conclude that the most appropriate technologies for deployment at the Bacton Energy Hub are the coupled Gas Heated Reformer and Autothermal Reformer or Non-Catalytic Partial Oxidation. These technologies are mature, demonstrated and well optimised at the scale required in this study.

We also acknowledge that, since the two technologies are broadly comparable in terms of process performance, the actual selection is likely to be governed by the specific makeup of the project consortium, with various parties bringing their own expertise and preferred solutions to the project. We have not explicitly considered cost in this assessment, however we understand that the Levelised Cost of Hydrogen produced by both technologies, once integrated into an overall process, is largely comparable. Hence, there is no significant cost driver for one over the other. Despite this, we recommend that future work undertake a rigorous cost assessment and LCOH analysis to identify any opportunities for cost saving and ensure the least-cost production technology is selected, subject to other project factors.

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