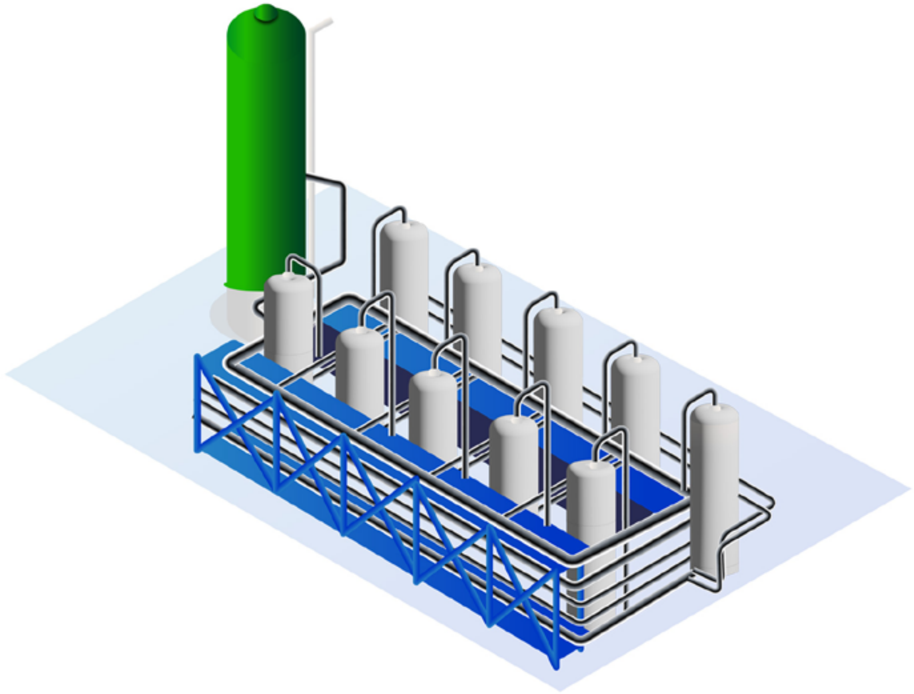
Low Carbon Hydrogen Production Through Methane Reforming

Introduction

Alongside ‘green’ hydrogen, produced through electrolysis using renewable electricity (see Electrolysers fact sheet), there may also be a significant role in Scotland’s future hydrogen economy for hydrogen produced using methane. This reforming chemical reaction has the advantage of being based on well-known technologies that have been used across the world for decades to produce hydrogen for industrial use.

Traditionally, reforming has used a natural gas feedstock and has entailed significant carbon dioxide emissions. However, adding Carbon Capture and Utilisation or Storage (CCUS) means that this process can be very low carbon (with the output often termed ‘blue’ hydrogen), and if a biological source of methane is used, emissions can even become zero or negative. These processes could enable production of hydrogen at competitive prices in the short to medium term, accelerating the delivery of a hydrogen economy.

Low carbon hydrogen through methane reforming also provides an excellent opportunity for Scotland’s supply chain to apply their products and services to a technology area with a very high degree of transferable skills. The primary technology, Steam Methane Reforming, is detailed in this fact sheet along with a similar alternative process, Autothermal Reforming.



Hydrogen Recovery and Purification by Pressure Swing Adsorption (PSA)

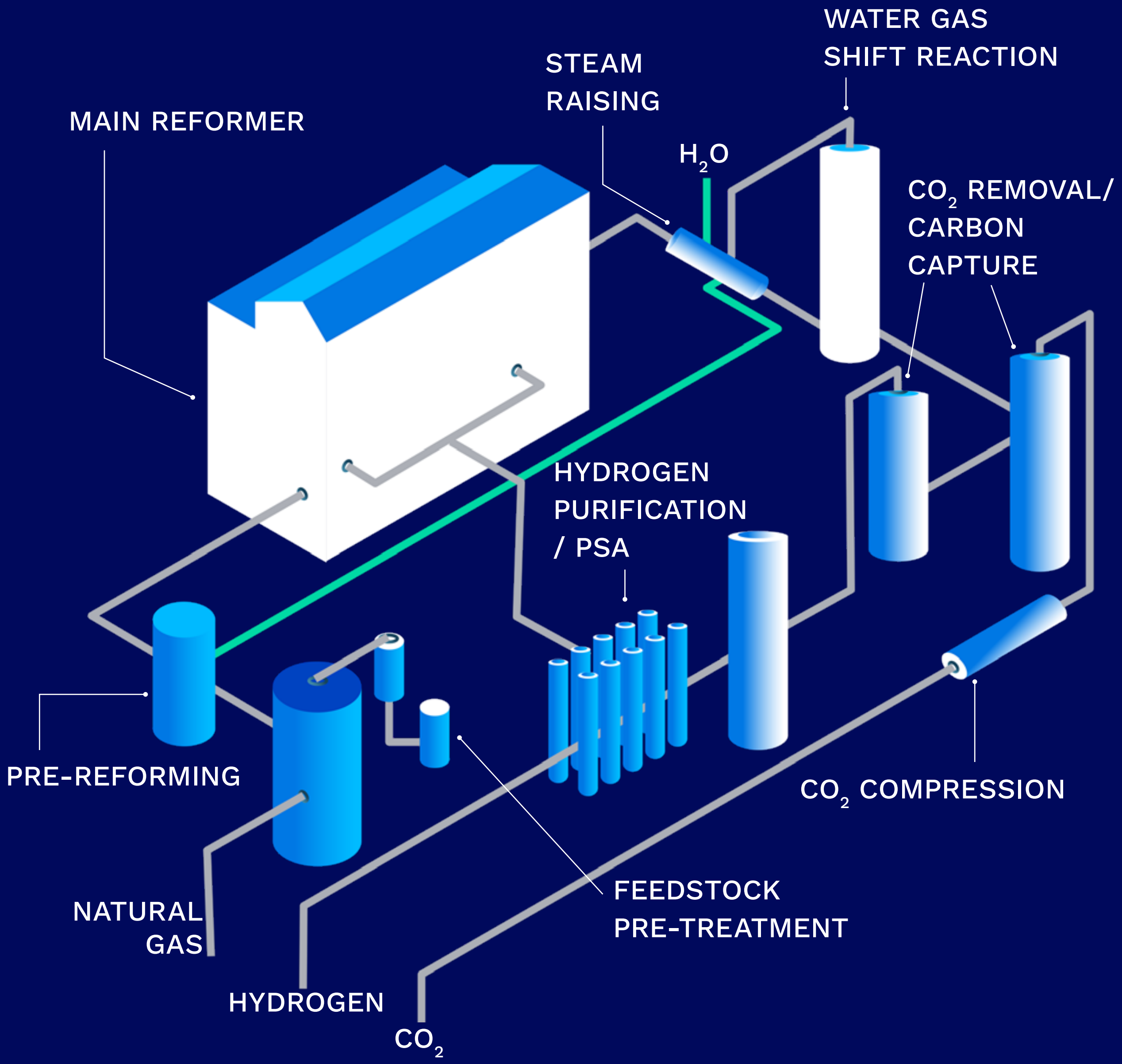
Steam Methane Reforming Process Summary

In the Steam Methane Reforming (SMR) process, natural gas or biomethane are combined with high temperature steam at elevated pressures, typically 15 - 30 bar, to produce hydrogen and carbon monoxide, or syngas. The syngas is further processed to yield additional hydrogen and carbon dioxide. The process is highly endothermic, requiring large amounts of process heat to drive the reforming reactions.

SMR is currently the process of choice for industrial scale hydrogen production and large-scale plants usually produce in excess of 100 tonnes H_2 / day. At present these SMR plants rarely include carbon capture, making this process, known as 'grey' hydrogen production, very carbon intensive. However, the carbon dioxide produced during SMR can be captured and stored to make this process a potential route to low carbon, 'blue' hydrogen production. When renewable biomethane is the feedstock, this process can even become carbon negative.

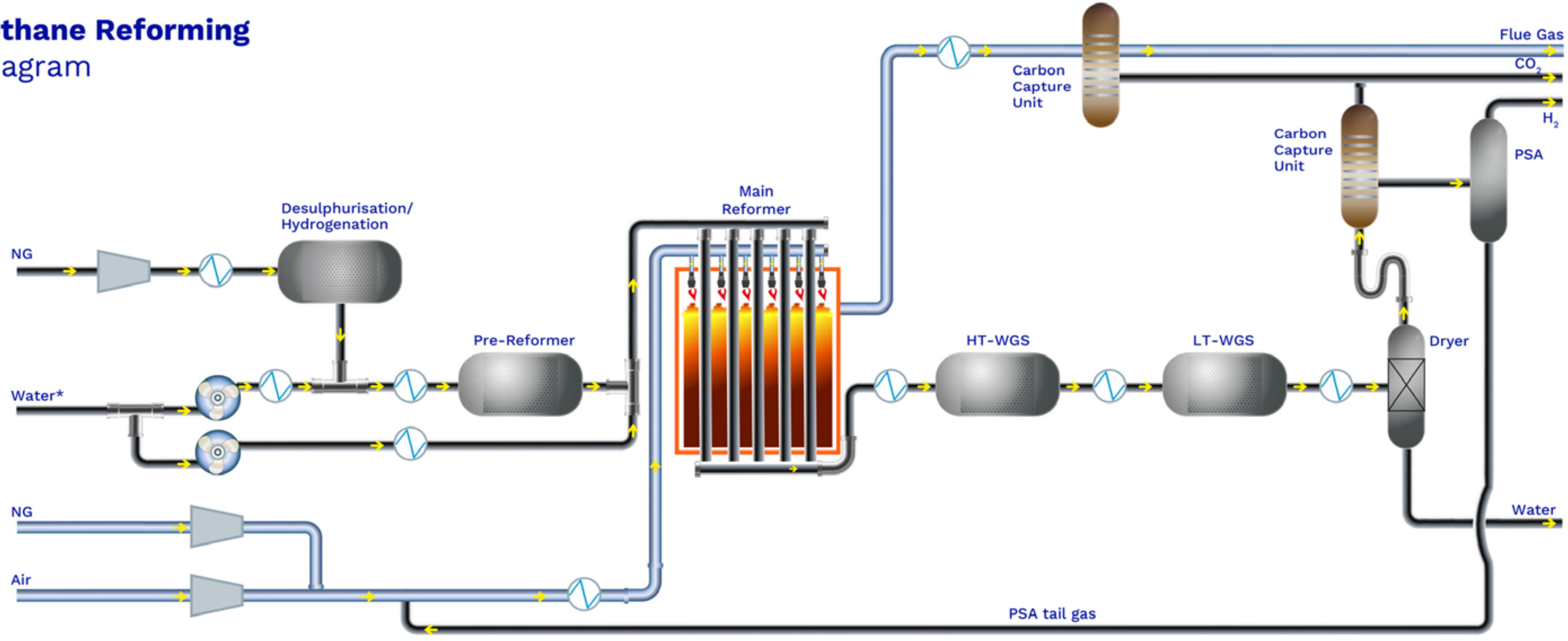
Thanks to innovation in process intensification, there is also now increasing interest in small scale, containerised, SMR solutions. These are capable of producing anywhere from 0.1 to 10 tonnes H_2 / day and could be particularly suitable for decentralised hydrogen production, utilising, for instance, renewable biomethane feedstock.

The Steam Methane Reforming process contains many individual process steps, as can be seen in the process diagram. We will focus on each individual step in this fact sheet.



Steam Methane Reforming

System Diagram



*Purified/De-Ionised Water

Feedstock Pre-Treatment

The natural gas or biomethane feedstock needs to purified before it enters the reforming process. The feedstock gases usually contain sulphurous and chlorinated compounds, which can poison and deactivate the catalysts that are used during reforming and shift reactions and must thus be removed.

Desulphurisation / dechlorination unit

Removal of the sulphur and chlorine impurities is performed in a hydrogenation reactor, where sulphur compounds react over a catalytic bed (usually based on molybdenum and cobalt sulphides) with hydrogen at 200-400°C to form Hydrogen Sulphide (H_2S). Chlorinated compounds are simultaneously converted into Hydrogen Chloride (HCl). Any unsaturated hydrocarbons in the feedstock can also be converted to their saturated counterparts during this process step.

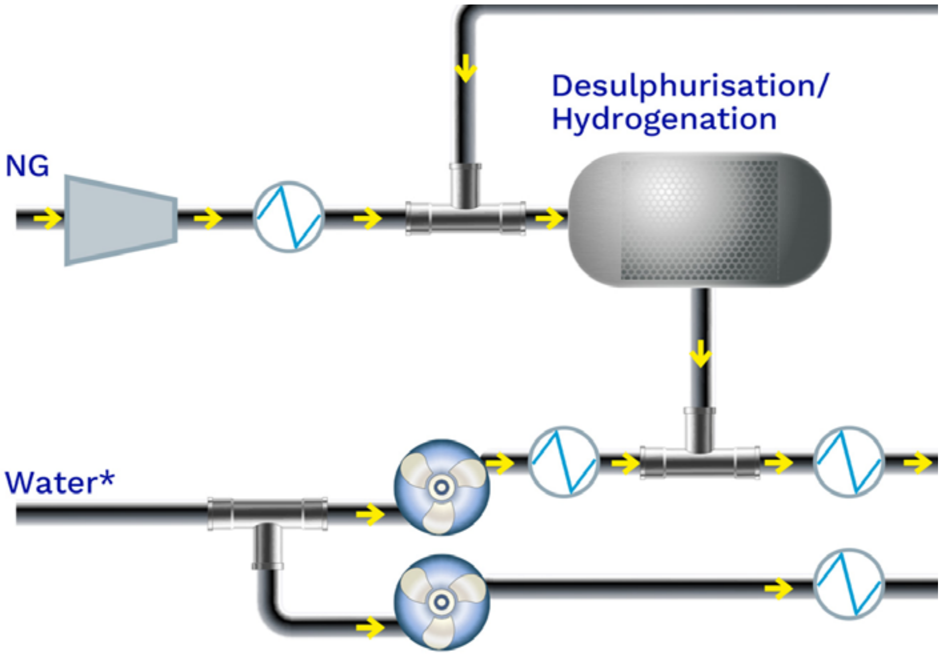
In a subsequent packed bed reactor, usually filled with Zinc Oxide (ZnO) and/or Sodium Oxide (Na_2O) these compounds are chemisorbed on the packed bed to form non-volatile Zinc Sulphide (ZnS) and Zinc Chloride ($ZnCl_2$) or Sodium Chloride (NaCl).

Steam Raising

The other feedstock to the reforming process is high temperature and pressure steam. Steam is usually generated in multiple heating steps, utilising waste heat from processes downstream resulting in steam with a pressure of 20 - 25 bar and a temperature of 400 - 600°C before entering the pre-reformer and main reforming reactors.

Water pre-treatment

Water for the reforming reactions needs to be purified, as any impurities can cause corrosion and scaling within the reactor equipment. De-ionisation is usually performed to remove any inorganic impurities, and reverse osmosis can be performed for any further purification. If non-mains water is used, additional particulate filters of Polypropylene (PP) or Polyvinyl Chloride (PVC) mesh may be required.



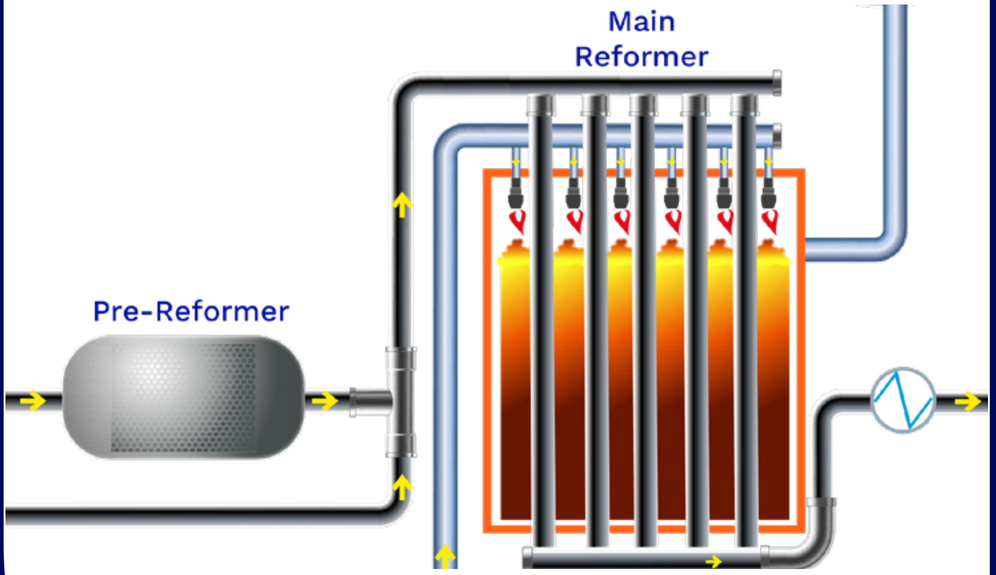
Pre-Reformer

Although not strictly necessary, a pre-reforming step is usually performed in order to enhance overall process efficiency. During the pre-reforming process, heavier hydrocarbons (compounds of hydrogen and carbon) found in the feedstock are converted to syngas and methane. This process is performed over a catalyst – Nickel (Ni) based catalysts are most commonly used, although small amounts of precious metals may be used to suppress any carbon formation. Pre-reforming is carried out at a lower temperature than the main reforming process – typically between 400 and 600°C. Carrying out the pre-reforming step can result in a reduced undertaking for the main reformer and consequently reduced energy consumption across the production process.

Main Reformer

After the pre-reforming step, additional steam is added to the process feed and, for the methane reforming reaction to occur, the reaction mixture is heated to 700 - 900°C. The heat for the reaction is usually supplied by multiple burners inside a furnace housing which are fuelled separately by natural gas or biomethane, whilst the reactant gas and steam mixture is fed through a multi-tubular reactor array which is packed with reforming catalyst. This catalyst is typically a nickel-based material, which is effective and economical. The main reforming reaction is $\mathbf{CH_4+H_2O \rightarrow CO+3H_2}$ (Methane + Water → Carbon Monoxide + Hydrogen).

A number of side reactions can occur during the process, one of which is coking, leading to carbon deposits and resulting in deactivation of the catalyst. In addition, carbon deposits can cause the mechanical blockage of tubes valves and manifolds. To prevent coking, the reforming process must be carried out using excess steam. Usually a steam/carbon ratio of 2.5 – 3 is used, where 1 is stochiometric.



Water Gas Shift

The product from the reforming reaction is syngas – a mixture of predominantly carbon monoxide and hydrogen. The carbon monoxide is converted into carbon dioxide and hydrogen by reacting with residual steam leaving the reformer. This is called the Water Gas Shift (WGS) reaction.

WGS is usually performed in two steps, at consecutively lower temperatures. In the first, High Temperature WGS, 95-98% of carbon monoxide is converted to carbon dioxide at temperatures of approximately 300-350°C over an Iron(III) oxide or ferric oxide (Fe_2O_3) catalyst. The second stage, Low Temperature WGS, reduces the carbon monoxide content further to c. 0.1 mol% by reacting over a copper (Cu), Zinc (Zn), or an Aluminium (Al) catalyst at approximately 180 - 250°C.

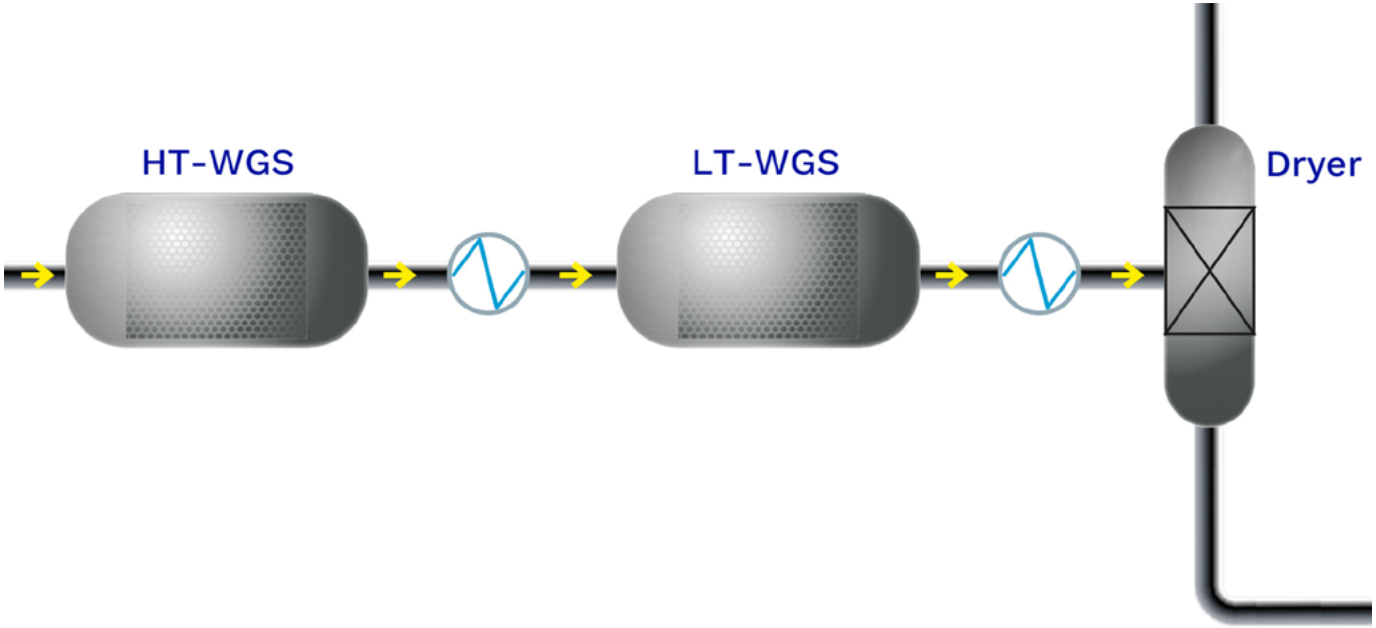
Preferential Oxidation and Drying

Preferential Oxidation, PrOX

Preferential Oxidation, PrOX - If further reductions of the carbon monoxide content in the process stream is required, preferential oxidation (PrOX) can be carried out as an optional process step, reducing carbon monoxide levels to ppm levels. Oxidation of the carbon monoxide is achieved by a reaction with oxygen, however highly selective catalysts are required to avoid oxidation of the hydrogen at the same time. This is typically done in a reactor packed with copper (Cu), gold (Au) or platinum (Pt) with either ceric oxide (CeO_2) or aluminium oxide (Al_2O_3) supports.

Water removal – dryer

Any unreacted water is now removed as its presence can make separation of other components downstream more difficult. Most commonly, the majority of water is removed by condensing from the product stream in a separating column.

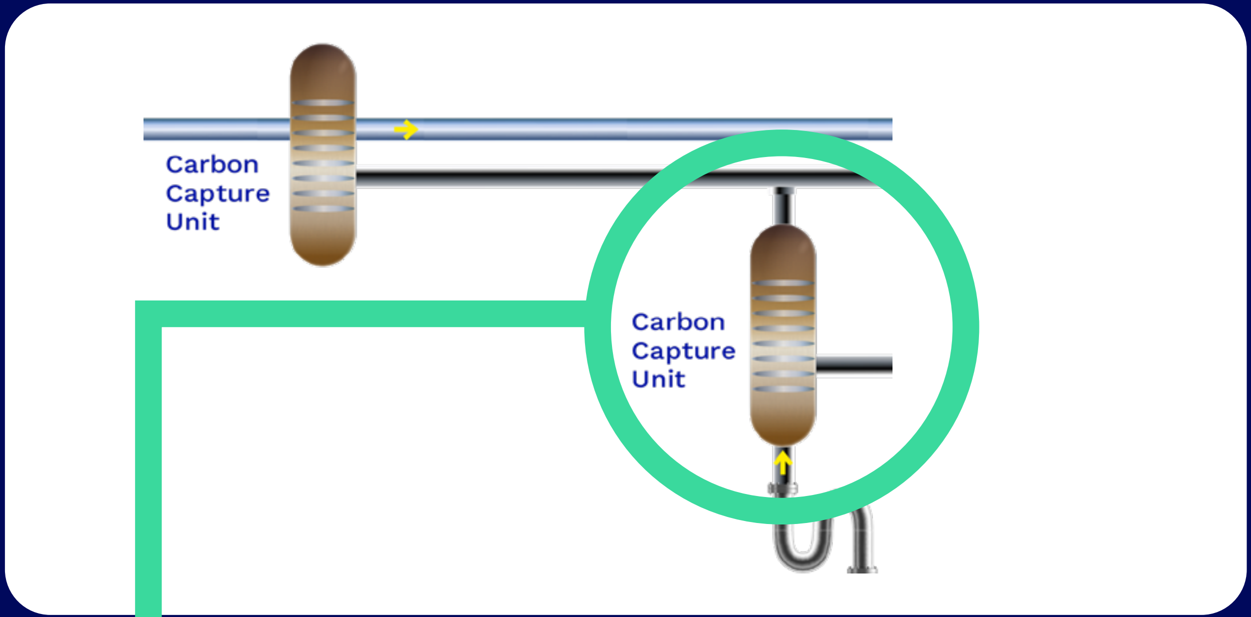


Carbon Capture

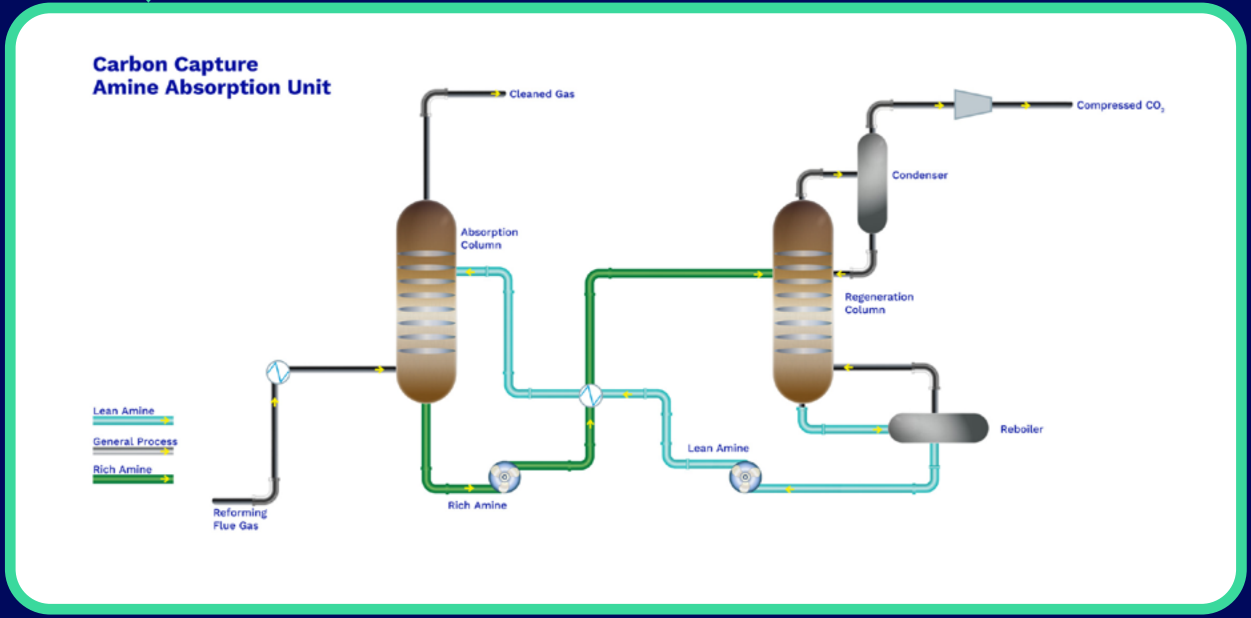
The steam methane reforming (SMR) process generates carbon dioxide (CO_2) at two distinct process steps: as a product of the SMR/WGS reactions and in the flue of the main reforming furnace, where natural gas or biomethane are burned to provide heat for the endothermic SMR reaction. Depending on the feedstock, carbon capture must be performed in the process stream to ensure CO_2 emissions are minimised. With regards to reactant CO_2: due to the high partial pressure of CO_2 post WGS and before hydrogen purification, this is usually chosen as the optimal point to incorporate it within the overall SMR process. CO_2 from the main reformer flue must be captured separately.

Carbon capture is an optional process step if the SMR feedstock is a renewable, biogenic carbon source, such as biomethane derived from biowaste, resulting in net zero emissions. If the carbon is captured and sequestered, the overall process becomes carbon negative. The most common and mature method of CO_2 removal from a gas stream is through amine absorption. CO_2 is selectively absorbed by an amine containing liquid at low temperatures (c. 40°C) and ideally elevated pressures in an absorption column. The amine leaving this column and which is now loaded with CO_2, is subsequently regenerated in another column, operated at higher temperature (c. 100°C) and reduced pressure, releasing the concentrated CO_2 stream at the top of the column. Any moisture is separated through a condensing trap. Capture rates of 90% are typical. Another method of capturing CO_2 that has been used at scale is Vacuum Swing Adsorption (VSA), which is similar in operation to Pressure Swing adsorption (PSA) (see the Hydrogen Purification section).

The highly pure carbon dioxide (CO_2) which is generated from the amine carbon capture unit is now compressed or liquefied to be transported for long term storage, sequestration or utilisation. An additional drying step may be required to remove trace amounts of water.



The image above illustrates where the carbon capture units are situated within the whole system diagram for SMR. The image below provides further detail of what each of those carbon capture units are comprised of.



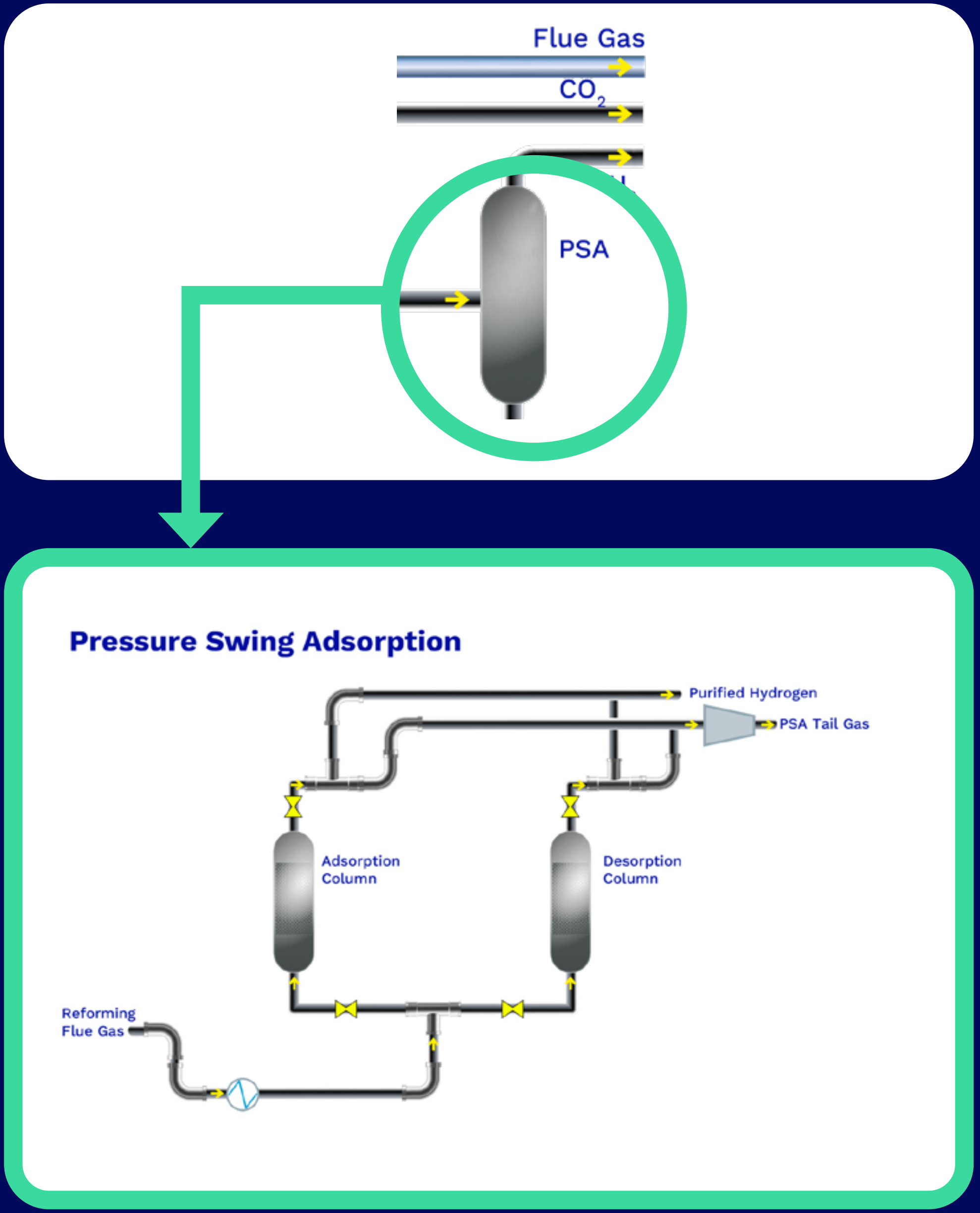
Hydrogen Separation And Purification

The final hydrogen product needs to be purified to be used in its final application. Regardless of whether carbon capture is performed or not, the process stream will contain carbon dioxide, and small quantities of carbon monoxide as well as unreacted natural gas, and these need to be removed. Different levels of purity are required, depending on the final application. A purity of 99.995% is typically required in transport applications such as Fuel Cell Electric Vehicles, but requirements are lower for hydrogen as fuel in boilers or burners for domestic, commercial or industrial heat.

Pressure Swing Adsorption (PSA)

The most common process for hydrogen separation and purification is Pressure Swing Adsorption (PSA). In this process, the impurities are alternately adsorbed and desorbed in multiple adsorption columns packed with solid adsorbents which have a high surface area, and by changing the process pressure. Due to the dynamic nature of the process, with columns continually alternating between adsorption and desorption, a minimum of 2 columns is required, but often as many as 10 columns are required to achieve sufficient purity and recovery.

Carrying out carbon capture prior to PSA means a large reduction in carbon dioxide content arriving in the PSA step. This allows for a reduction in equipment size and adsorbent quantity, reducing overall capital expenditure and increasing separation efficiency.

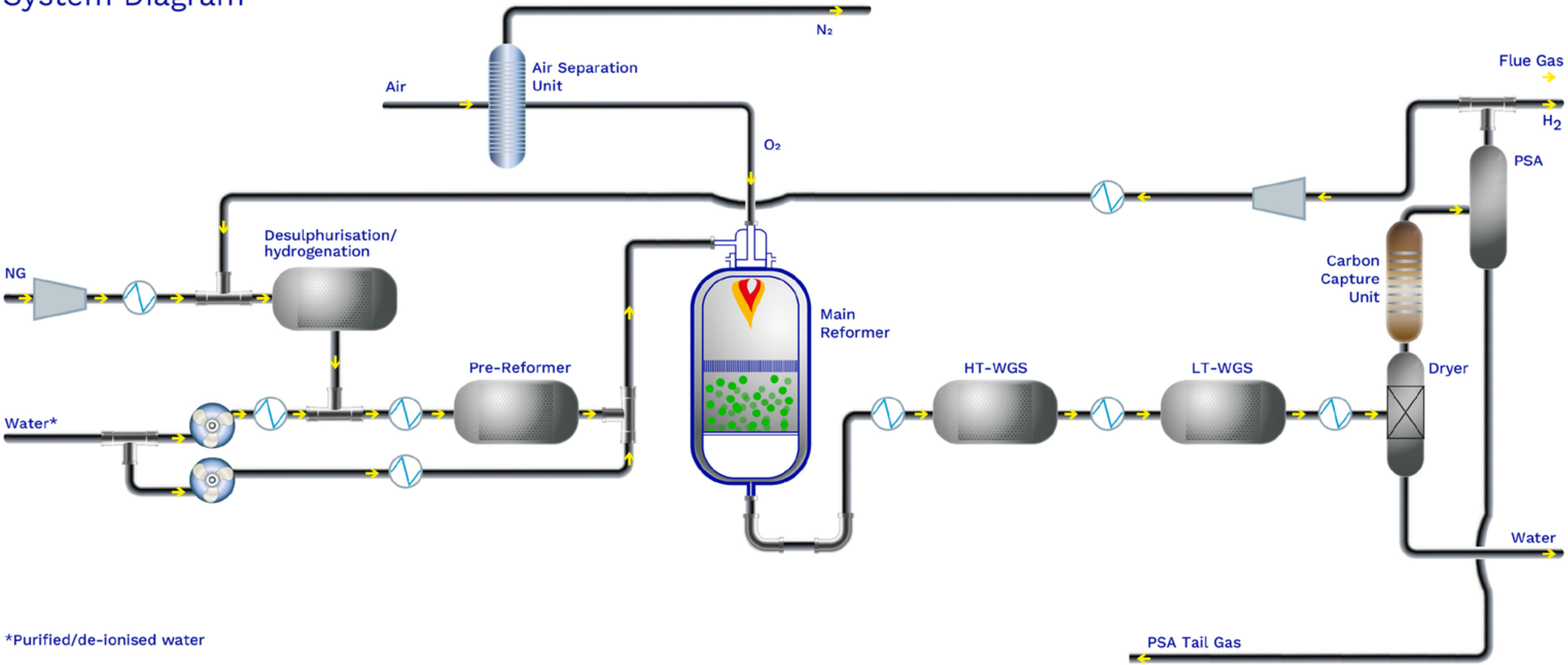


Autothermal Reforming Process Summary

Autothermal Reforming (ATR) of natural gas or biomethane is an alternative route to production of low carbon hydrogen. The process combines Steam Methane Reforming (SMR), and partial oxidation. The overall ATR process is very similar to SMR but can offer a number of advantages. The key difference between the two processes is the main reforming reaction, which in the case of ATR takes places in the presence of both steam and oxygen, but at higher pressure and temperature than SMR, typically 30 –100 bar and 900 –1,050°C, similarly producing carbon monoxide and hydrogen or syngas. Unlike SMR however, the majority of the heat required for the reforming is provided internally by the exothermic partial oxidation of methane and thus the overall reforming process is close to thermoneutral. Because there is no need for heat to be provided by burners, all the CO_2 is generated by the chemical reaction process, simplifying the Carbon Capture process as there is no flue gas. Other benefits are the higher operating temperature allowing for more heat recovery. However, a major disadvantage of ATR is the need for pure oxygen or enriched air, requiring an air separation unit as part of the process. This is a major capital expenditure and is only economically viable for large plants, which essentially precludes containerised versions of ATR, unless the process is integrated with another source of pure oxygen, such as water or steam electrolysis.

Autothermal Reforming – Main Reformer

Autothermal Reforming
System Diagram

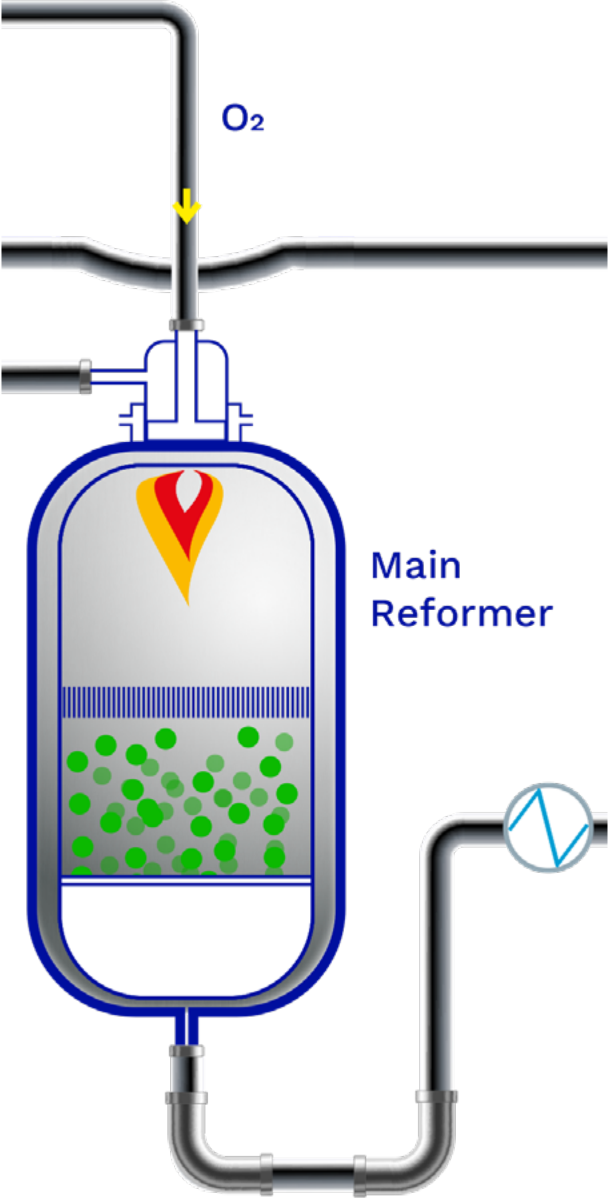


*Purified/de-ionised water

Main Reformer

The main autothermal reforming reaction takes place at 900 –1,050°C, at pressures of 30–100 bar. The bulk of the heat required for the reaction is supplied by partial oxidation of methane by pure oxygen or enriched air, which is supplied by an Air Separation Unit and fed to the reactor with the hydrocarbon/steam feed through a burner, where the mixture is ignited. Due to the internal heating from partial oxidation, the reactor design is simplified with a single packed bed, although typically packed with different catalysts in a layered system above a combustion section. A Ni based catalyst is the main reforming catalyst, with small amounts of other precious metal-based catalysts, added depending on application. As is the case for SMR, a number of side reactions are possible in the presence of Ni and carbon formation in particular needs to be avoided. The presence of oxygen and the higher reaction temperature alleviate the risk of coking, which means that the steam/carbon ratio is usually much reduced compared to SMR and can be as low as 0.6 for the main reforming reaction. This translates into a much-reduced duty for the steam generator, saving on capital and operational cost.

A typical ATR reaction is: **$4CH_4 + 2H_2O + O_2 \rightarrow 4CO + 10H_2$**, but different reaction stoichiometries are possible.



STEAM METHANE REFORMING (SMR)

Process Component	Sub-component	Material(s)	Specs
Feedstock Pre-Treatment			
	Specialist catalysts and absorbent materials	Modified molybdenum disulphide (MoS_2) and Cobalt (Co)	
		Zinc Oxide and Sodium Oxide (ZnO and Na_2O)	
		Alumina support materials for catalysts	Can come in different forms including extruded pelets and spherical beads but also more complex forms, such as Rashig rings for high surface area and low pressure drop.
	Reactor Vessel	Stainless steel	Suitable under operating conditions e.g. AISI 316L or AISI 304L
Steam Raising			
Steam Generator Vessel (rated at operation pressure		Stainless steel	e.g AISI 316L, AISI 304L, AISI 516 - Materials and wall thickness dependent on operating conditions
		Corrosion resistant superalloys	e.g Inconel 600
	ASME Boiler &Pressure Vessel Code		
	Heat Exchanger		Typically tube shell
	Electrical heating elements or burners		
Particulate Filters (if non-mains water used)		Polyproylene (PP) or Polyvinyl chloride (PVC) mesh	
	De-ionising resin		
	Ion Exchange Membranes		
	Ion Exchange Salts		
	Containers	Polymer or Steel	
	Water pumps		
	Buffer Tanks	Polyproylene (PP) or Polyethylene (PE)	
	CO_2 Scrubber	Polyethylene (PE) composite material	
Reverse Osmosis	Membrane filtration unit for ultrafiltration	Nanoporus membranes	1 nm pore size
	High pressure water pump		

STEAM METHANE REFORMING (SMR)

Process Component	Sub-component	Material(s)	Specs
Pre-reformer			
	Reactor Vessel	Stainless steel vessels	Suitable under operating condition or specialist high temperature e.g. AISI 316L or AISI 304L
		Corrosion resistant alloys	
		Adiabatic, packed bed reactor	
	Catalyst	Nickel (Ni) based catalyst - most common	
		Can sometimes be precious metal catalyst - Platinum (Pt), Rhodium (Rh), or Ruthenium (Ru) and lanthanides, Ceric Oxide (CeO_2), Lanthanum(III) oxide (La_2O_3)	
	Specialist catalysts and support materials	Alumina support materials for catalysts	Can come in many forms, such as extruded pellets, spherical beads, but also more complex forms, such as Rashig rings for high surface area and low pressure drop
		Ferrochromium (FeCr) alloy for monolith substrates	
Main Reformer			
	Specialist catalysts and support materials	Nickel (Ni) based catalyst most common	
		Alumina support materials for catalysts	Can come in many forms, such as extruded pellets, spherical beads, but also more complex forms, such as Rashig rings for high surface area and low pressure drop
		Ferrochromium (FeCr) alloy for monolith substrates	
	Reactor Vessel	Multi-tubular packed bed reactor (NiChrome (NiCr) steel alloy), or Modified HP alloys with higher Nickel (Ni) content and small additions of Niobium (Nb)	HK40(ASTM A351 and , OD 75-125 mm, length up to 15 metres in 3m welded sections (much reduced dimensions for containerised option)
	Furnace Enclosure	Specialist application	
		High temperature natural gas burners, directed laterally or vertically to heat tubes	

STEAM METHANE REFORMING (SMR)

Process Component	Sub-component	Material(s)	Specs
Water Gas Shift			
High Temperature Shift	Reactor Vessel	Standard adiabatic stainless steel	Steel grade suitable under operating conditions e.g AISI 361L or AISI 304L
	Specialist catalysts and support materials	Iron (III) Oxide (Fe^2O^3) catalysts	
		Alumina support materials for catalysts.	Can come in many forms, such as extruded pellets, spherical beads, but also more complex forms, such as Rashig rings for high surface area and low pressure drop
Low Temperature Shift	Reactor Vessel	Standard adiabatic stainless steel	Steel grade suitable under operating conditions e.g AISI 361L or AISI 304L
	Specialist catalysts and support materials	Copper (Cu), Zinc (Zn) or Aluminium (Al) based catalysts	
		Alumina support materials for catalysts	Can come in many forms, such as extruded pellets, spherical beads, but also more complex forms, such as Rashig rings for high surface area and low pressure drop
Preferential Oxidation and Drying			
Preferential Oxidation	Specialist catalysts and support materials	Copper (Cu), Gold (Au), Platinum (Pt) on Ceric Oxide (CeO_2) and/or Aluminium Oxide (Al_2O_3) catalysts	
		Alumina support materials for catalysts.	Can come in many forms, such as extruded pellets, spherical beads, but also more complex forms, such as Rashig rings for high surface area and low pressure drop
	Reactor Vessel	Adiabatic packed bed reactor	
		Stainless steel vessels	Steel grade suitable under operating conditions e.g AISI 361L or AISI 304L
Water Removal	Water Separation Column	Presence of concentrated hydrogen at elevated pressure makes a low strength/highly ductile steel preferable	e.g AISI 361L

STEAM METHANE REFORMING (SMR)

Process Component	Sub-component	Material(s)	Specs
Carbon Capture			
	Drying unit		
	Compression and refrigeration equipment		CO_2 liquefies on adiabatic expansion from a critical pressure of c. 74 bar and cooling to a critical temperature of 31°C, requiring minimum active refrigeration. Alternatively, it can be cooled to −50°C at 7 bar
	Pressure vessels or gas bottles		Able to withstand pressures up to 200 bar
	Separation columns	Multi-stage absorption and regeneration stainless steel columns	e.g AISI 361L or AISI 304L
		Perforated plates separating stages	
		Condenser	
		Reboiler	
	Amine buffer/storage vessel		
	Specialist absorbent material	Amine containing liquid, such as aqueous solutions of Monoethanolamine (MEA) or Methyldiethanolamine (MDEA)	
Hydrogen Separation and Purification			
Pressure Swing Adsorption, PSA	Packed Bed Columns	Stainless steel	e.g AISI 361L or AISI 304L
	Specialist adsorbent materials	Aluminosilicates / Zeolites	
		Alumina binders	
Hydrogen compressors	Reciprocating compressors for typical storage pressures and throughout		
	Pressure monitoring (transducers)		
	Pressure vessels for storage		

AUTOTHERMAL REFORMING (ATR)

Process Component	Sub-component	Material(s)	Specs
Pre-reformer			
Reactor Vessel		Stainless steel vessels	Suitable under operating condition or specialist high temperature e.g. AISI 316L or AISI 304L
		Corrosion resistant alloys	
		Adiabatic packed bed reactor	
	Gas Heated Reformer reactor (GHR)	Multitubular array within reactor vessel, with heat supplied externally to internal tubes by gas exiting main reformer	Tube-shell heat exchange configuration. Tube material suitable for high temperatures, such as AISI 316L, AISI 316Ti
		specialist high temperature, corrosion resistant alloys	
	Catalyst	Nickel (Ni) based catalyst - most common	
		Can sometime be precious metal catalyst - Platinum (Pt), Rhodium (Rh), or Ruthenium (Ru)	
		Lanthanides, Ceric Oxide (CeO_2), Lanthanum(III) oxide (La_2O_3)	
	Specialist catalysts and support materials	Alumina support materials for catalysts	Can come in many forms, such as extruded pellets, spherical beads, but also more complex forms, such as Rashig rings for high surface area and low pressure drop
		Ferrochromium (FeCr) alloy for monolith substrates	

AUTOTHERMAL REFORMING (ATR)

Process Component	Sub-component	Material(s)	Specs
Main Reformer			
	Specialist catalysts and support materials	Nickel (Ni) based catalyst most common	
		Alumina support materials for catalysts	Can come in many forms, such as extruded pellets, spherical beads, but also more complex forms, such as Rashig rings for high surface area and low pressure drop
		Ferrochromium (FeCr) alloy for monolith substrates	
Reactor Vessel	Single two stage reactor - top stage		
Reactor Vessel	Single two stage reactor - bottom stage	Nickel-chromium (NiCr) steel alloy, e.g. Modified HP alloys with high Nickel (Ni) content and small additions of Niobium (Nb)	Demanding operating conditions require highly oxidation resistant steel alloys
Reactor Vessel			Internal reactor walls lined with refractory materials, e.g. Aluminium Oxide (Al_2O_3) tiles, acting as heat shield
Reactor Vessel	High temperature burner at the top of the reactor including Oxygen/Feul - pre-mixing		

Balance of Plant and Safety Equipment

Hydrogen production through SMR or ATR is a multistep, interdependent process which requires careful control in order for each process step to operate within acceptable process parameters and at optimum efficiency. For optimum process efficiency, a high level of process integration, and in particular thermal integration, is essential, to minimise heat losses and thus unnecessary energy consumption.

Balance of Plant

Heat Exchangers	Solenoid or pneumatic on/off switches	Electrical safety and interlocks
Steam Turbines	Multidirectional valves	Shipping containers
Compressors	Ball valves	Acoustic shielding
Blowers	Pressure relief valves for process pressure control and monitoring	Steel construction frames
Liquid/Water Pumps	Stainless steel pipework (AISI 316	Stairways, handrails and safety barriers
Pressure gauges for visual inspections	Compression fittings or orbital welded fittings	Concrete foundations and plinths
Pressure transducers for pressure monitoring	Process control systems	Earthing and drainage
Back pressure regulators	Electrical supplies for componentry	Skids
Thermocouples and thermistors for temperature monitoring	Electrical heating elements	Drainage to remove rainwater or maintenance cleaning water
Mass flow controllers to control mass reactant flow	Electrical signalling for control systems and	Sampling of feedstock chemical composition
Control valves	Electrical switchboard and electronics cabinets	

Safety

SMR and ATR projects will need to make sure they comply with the minimum health and safety regulations – for example the Dangerous Substances and Explosive Atmospheres Regulations (DSEAR). Supply chain opportunities will exist relating to maintenance and inspection services for both invasive and non-invasive inspections. Divergence from expected performance may indicate issues with catalysts.

Safety measures can be integrated with process controls and would include warning signs (illuminated), pressure and temperature monitoring linked to pressure relief valves and burst valves installed for critical pressure increases to avoid equipment damage or explosions. Both fixed location and handheld mobile gas detection devices will also be required for monitoring purposes. And containerised processes will also require extraction and ventilation systems to prevent the build-up of flammable mixtures inside enclosed spaces.

Scottish Enterprise

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