SMR HYDROGEN YIELD IMPROVEMENT AND CO_2 EMISSIONS REDUCTION USING CRYOGENICS

Refinery at Port Jerome sur Seine, France

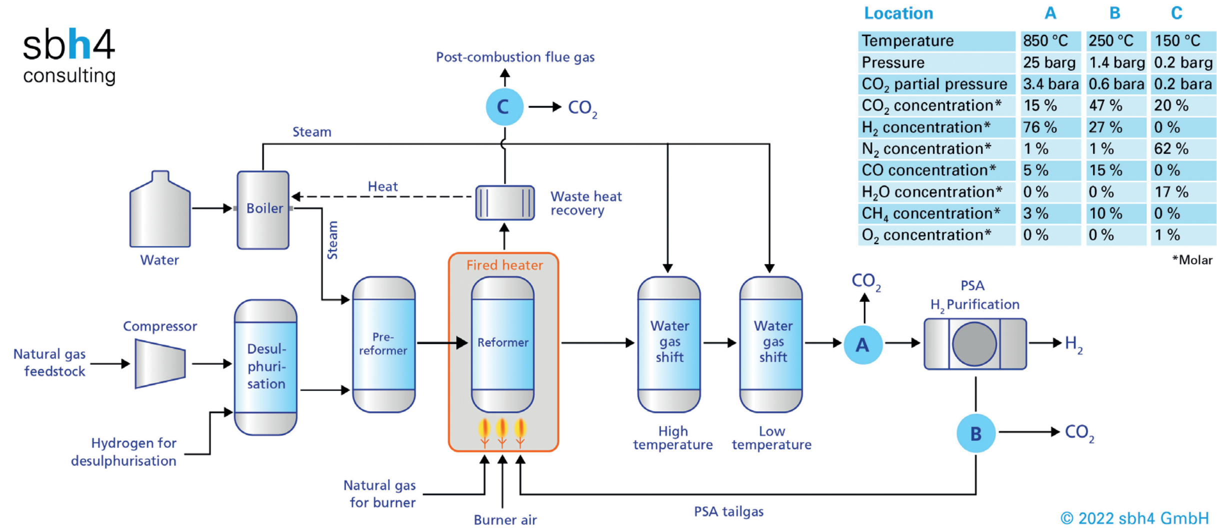
Much has been said about CCS – carbon capture and storage. The need to decarbonise is clear. Renewable power generation and green hydrogen may do much of the heavy lifting when they scale up in coming decades, but there are many steam methane reformers (SMRs) existing on refineries that must also be decarbonised.

Steam methane reforming of natural gas, refinery gas or naphtha feedstocks is the most common process to produce hydrogen is. When these fossil fuels are used to generate hydrogen without capturing the CO_2 emissions, it is called 'grey' hydrogen. If most of the CO_2 from the SMR is captured, the hydrogen is referred to as 'blue'.

CO_2 is released from the SMR in two locations, firstly as the feedstock is transformed to hydrogen, CO_2 is produced within the process as a by-product. This is an unavoidable consequence of this chemical pathway. The second source of CO_2 emissions are from the combustion of fossil fuels, generally the same natural gas feedstock, to create the heat that is required to drive the reforming chemical reactions that convert the feedstock to hydrogen.

SMR at Port Arthur, Image courtesy of Air Products and Chemicals Inc

Potential Locations for CO_2 Capture from Steam Methane Reforming



Location	A	B	C
Temperature	850 °C	250 °C	150 °C
Pressure	25 barg	1.4 barg	0.2 barg
CO_2 partial pressure	3.4 bara	0.6 bara	0.2 bara
CO_2 concentration*	15 %	47 %	20 %
H_2 concentration*	76 %	27 %	0 %
N_2 concentration*	1 %	1 %	62 %
CO concentration*	5 %	15 %	0 %
H_2O concentration*	0 %	0 %	17 %
CH_4 concentration*	3 %	10 %	0 %
O_2 concentration*	0 %	0 %	1 %

*Molar

	Location A	Location B	Location C
Process stage	Pre-PSA	Post-PSA	Post-combustion
Advantages	High pressure, high CO_2 concentration, highest CO_2 partial pressure, lowest unit cost of CO_2 capture from Amine Solvent or VSA processes	Low flowrate (H_2 removed), highest CO_2 concentration	More than 90 % capture rate possible (captures process CO_2 and burner CO_2 emissions), low pressure location can be suitable for emerging CO_2 capture technologies such as TSA and mineralisation
Disadvantages	Max 70 % CO_2 capture rate possible (burner CO_2 emissions not captured), high flowrate (H_2 included)	Max 70 % CO_2 capture rate possible (burner CO_2 emissions not captured), low pressure	Low pressure, lowest CO_2 concentration, high flowrate due to combustion air, highest unit cost of CO_2 capture from Amine Solvent or VSA processes

CO_2 capture from steam methane reformers (SMRs) is often regarded as a 'quick-win' in the decarbonisation of industrial processes. The CO_2 concentration, pressure, and partial pressure in the SMR process gas is high. This leads to cost-effective CO_2 capture. Furthermore, CO_2 has been captured from SMRs for decades so that the CO_2 can be used to make urea fertilizer, when reacted with ammonia that is produced from hydrogen made on the SMR. There is therefore a wealth of experience to leverage.

The use of cryogenics to capture and purify CO_2 from SMRs is likely to be the next milestone in the development of CO_2 capture from these units. The Cryocap™ H2 process from Air Liquide combines cryogenic separation of CO_2 from the SMR process gas stream with membrane separation of hydrogen.

A demonstration project at an SMR in Port Jérôme, on the river Seine in France, showed that an additional 12% hydrogen yield from the SMR is achievable using the Cryocap™ H2 process. This can have a tremendous positive impact on operational economics and can help to fund the investment in the Cryocap™ H2 equipment.

With Cryocap™ H2 directing more hydrogen to the product stream, there is less hydrogen available for the SMR fired heater, so additional natural gas is required to compensate for the reduced heat energy available. However, the additional hydrogen production can more than offset the cost of the additional natural gas.

If liquid CO_2 is required for food and beverage applications, additional CO_2 purification is required. In the Cryocap™ H2 process, oxygen is added to react with hydrogen in the CO_2

Steam Methane Reforming Chemistry

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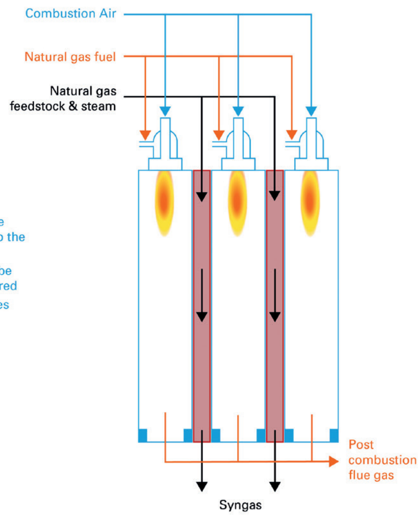

Notes:
- In the SMR the air/fuel combustion reaction takes place in a separate part of the equipment to the reforming reaction
- SMR may alternatively be side-fired or upwards-fired
- Red shaded area denotes catalyst bed

	Steam Methane Reforming – SMR
Carbon feedstock	Natural gas, refinery gas or naphtha
Oxygen input	Air for fuel combustion to heat the reforming process
Steam feedstock	From waste heat recovery boiler
Catalyst	Nickel
Target chemical reactions	$CH_4 + H_2O \rightarrow CO + 3H_2$
Additional side reactions	$CO + H_2O \rightarrow CO_2 + H_2$
Energy required/released	Endothermic, requires heat input
Hydrogen content in syngas	~70% H_2, balance CO, CO_2 and CH_4
Syngas pressure	15 to 40 bar, 25 bar is typical
Syngas temperature	850 °C
Downstream process	Water-gas shift: $H_2O + CO \rightarrow H_2 + CO_2$

Steam Methane Reforming Decarbonisation

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Notes:
- CO_2 is released from the reforming process chemistry
- CO_2 emissions are also associated with heat energy required to drive the reforming reactions
- The heating process can potentially be decarbonised with renewable power and electrical heating or microwaves
- CCS to capture CO_2 from the process and / or the associated heat energy production is possible

	Steam Methane Reformer SMR
Combustion reaction forming post-combustion CO_2	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
Chemical reaction producing CO_2 in process	$CH_4 + H_2O \rightarrow CO + 3H_2$ $CO + H_2O \rightarrow CO_2 + H_2$
Decarbonisation approach for CO_2 generated by the process	Feed the reformer with biomethane instead of natural gas or CO_2 capture
Industries with SMR applications	Ammonia, Methanol, Gas-to-Liquids, Refining

stream to produce water using catalytic oxidation. The water is then removed on regenerative dryer adsorption beds. Excess oxygen is separated from the liquid CO_2 using cryogenic distillation. Mercury removal is a final polishing stage which is achieved on an activated carbon filter bed.

CO_2 liquefaction is achieved using a heat exchanger to condense CO_2 gas. The cold side of the heat exchanger is generally fed with a refrigerant gas from a typical mechanical refrigeration circuit. Electrical power is required to operate the refrigeration equipment, so the process can be decarbonised using renewable electricity.

The CO_2 side of the liquefaction circuit is operated at a pressure of 15 to 25 bar. At elevated pressure, common refrigerant gases such as CO_2, ammonia or F-Gases can be used to achieve the temperature required to liquefy the CO_2.

As an alternative to mechanical refrigeration, ammonia absorption refrigeration can be used. This process avoids the mechanical compression of a refrigerant gas and derives the cold energy instead from the absorption and desorption of ammonia in water. To drive the ammonia out of the water, heat energy is required. If waste heat is available, this process can be more efficient than mechanical refrigeration.

After liquefaction, CO_2 is stored and transported in tanks which are insulated to minimise boil off. Typically, liquid CO_2 storage tanks are constructed of carbon steel and insulated with polyurethane foam. Often, a refrigeration unit is used to re-liquefy boiled off CO_2. This avoids CO_2 losses and over-pressurisation of the CO_2 storage tank.

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