VSA, membrane and PSA technologies for steam methane reforming CO2 capture

More than 95% of the current hydrogen production worldwide is derived from fossil fuels and Steam-Methane-Reforming is the dominant technology. Stephen B. Harrison, Managing Director, sbh4 consulting looks at some of the ways CO2 can be captured. www.sbh4.de

Methane and steam are converted into hydrogen and CO2 with a typical content of 76% hydrogen, 17% CO2, and 7% unreacted methane and other gases.

The SMR operates at pressures of up to 25 bar. To purify the hydrogen, a Pressure Swing Adsorption (PSA) unit is used, which takes advantage of the elevated pressure of the gases produced by the SMR. The tail gas from the PSA is fed back into the fired burners in the SMR, and its calorific value is used to enhance energy efficiency.

Under current practices, the CO2 is either released into the atmosphere or, in the case of hydrogen production for ammonia for fertilizers, the CO2 is captured to be reacted with ammonia to produce urea. In such applications, a water wash tower to cool the gas and remove particulates followed by a twin-tower amine-based CO2 absorption and CO2 stripping system is a common configuration to capture the CO2 gas.

As an alternative to amine-wash technology, VSA or PSA adsorption can be used to capture the CO2 gas. To employ these technologies in this way, there are two basic process flow sheet options to capture the CO2 content from the process gases leaving the SMR. In the first variant, the carbon dioxide is separated directly after the SMR, hence the hydrogen PSA only needs to separate additional impurities.

In a second process flow sheet option, the hydrogen PSA remains unchanged, and the CO2 is sequestered from the hydrogen PSA tail gas. This process flow sheet may be favourable due to the high CO2 concentration in the hydrogen PSA tail gas of more than 80%. Both process flow sheet options have been implemented in demonstration plants.

VSA CO2 capture

Air Products operates two SMR trains at their premises in Port Arthur, Texas. The purified hydrogen is fed into a 1,000 km long transmission pipeline with a capacity of 1.3 million Nm3/hr of hydrogen, which extends from Houston, Texas to New Orleans, Louisiana. It connects more than 20 industrial hydrogen users in a very efficient way.

To capture the CO2 content of the product gas Air Products opted for the first process flow sheet option and installed an additional PSA unit between the SMR and the hydrogen PSA unit. As it draws the high purity CO2 gas at sub-atmospheric conditions, it is also referred to as Vacuum Swing Adsorption (VSA).

In the VSA process, adsorber vessels are fed with high-pressure product gas. CO2 is selectively adsorbed onto the adsorbent bed. The hydrogen-rich gas which was not adsorbed is fed into the standard hydrogen PSA for further purification. Afterwards, the vessel undergoes a series of pressure equalisations with other vessels of lower pressure levels. The adsorber vessel contains now high-purity CO2. The CO2 gas is drawn out by an 'evacuation' step, which brings the pressure below atmospheric pressure. In a second step, blowdown gas is taken from a lower pressure bed, compressed, and fed back to a higher-pressure bed to 'rinse' the vessel. Both steps of 'rinse' and 'evacuation' are essential to achieve high CO2 purities.

More than 90% of the carbon dioxide is removed in each of the VSA trains. This equates to more than 1 million Tonnes of CO2 capture per year resulting in a major contribution to the decarbonisation of hydrogen production and industrial gases operations.

The CO2 is subsequently compressed in an intercooled 8-stage centrifugal compressor to 140 bar, which is about 70 bar above the critical pressure of CO2. A purpose-built 21 km long CO2 pipeline connects the VSA units at Port Arthur to an existing 60 cm diameter CO2 transmission pipeline with a total length of about 500 km. This transmission pipeline connects oil fields in Texas and Louisiana. Ultimately, the captured CO2 is used for Enhanced Oil Recovery (EOR) within these oil fields.

Membrane and PSA CO2 capture

Air Liquide has developed a CO2 sequestration process, based on the second process flow sheet option, for the CO2-rich tail gas from SMR hydrogen PSA units. The PSA tail gas is dried by means of an additional PSA. The gas stream is compressed to a pressure at which CO2 can be separated by liquefaction at around -50°C, close to the triple point. An additional control loop avoids freezing of CO2 under all operating conditions to avoid system blockages.

Within the cryogenic unit, partial condensation and distillation techniques are applied to separate the CO2 from impurities present in the stream. The non-condensable gases are fed to a cryogenic membrane system, where additional hydrogen and CO2 are recovered. This 'Cryogenic Capture' stage is unique to the Air Liquide process and gives its name to the technology, which is known as Cryocap™. It leads to an increased hydrogen productivity of 10-20%, as well as a CO2 recovery rate of more than 98%. All other residual gases are sent back to the burners in the reformer furnace, where their calorific value is utilised.

The high purity (>99.5%) CO2 stream leaves the cryogenic unit before it is further compressed to supercritical pressure. If food-grade CO2 is the requirement, hydrocarbon and methanol traces originating from the SMR process can then be removed in a final purification step.

The first of its kind Cryocap™ demonstration installation in Port-Jérôme at a large-scale hydrogen SMR has a CO2 capture capacity of 100k Tonnes / year. Since 2013 Air Liquide has been planning to install a Cryocap™ unit at its Rozenburg SMR in the Netherlands, which would have a capture capacity of 500,000 Tonnes of CO2 per year. In 2020 Air Liquide applied for government funding within the SDE++ grant scheme to ensure the economic viability of this scheme. If the final investment decision is taken in 2021, the project could start capturing and storing CO2 by 2024.