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## Achieving 95% direct CO<sub>2</sub> reduction for hydrogen plants

Decarbonisation solutions targeting existing refinery hydrogen plants enable refiners to achieve long-term CO<sub>2</sub> capture while minimising site space requirements and capital

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### Based on decades of reforming experience, solutions using ADVANCED REFORMING<sup>™</sup> technologies can be integrated into existing hydrogen plants for 95% carbon dioxide (CO<sub>2</sub>) reduction.<sup>1</sup>

The syngas industry can reduce its  $CO_2$  emissions using innovative solutions for the energy-efficient production of hydrogen, ammonia, and methanol that are demonstrated at scale and available today.

Conventional, or grey, syngas production uses a steam methane reformer (SMR) to convert gasified coal, natural gas, and other hydrocarbon based feedstocks into a mixture of hydrogen and carbon monoxide. The hydrogen produced via this process is used for petroleum based clean fuel, ammonia fertiliser, and methanol production.

The syngas carbon monoxide (CO) can be used to produce chemicals, fuel, and energy, or additional hydrogen ( $H_2$ ) via the water gas shift (WGS) reaction. While syngas production through the decades has focused on reducing production cost, attention is now on reducing green-house gas (GHG) emissions to meet 2050 net-zero CO<sub>2</sub> emissions targets.

Broadening the use of proven **ADVANCED REFORMING** technologies, as well as  $CO_2$  capture, utilisation, or storage technologies (CCUS), can significantly reduce the carbon intensity of syngas production. These CCUS technologies use existing technology and materials, manufacturing, and supply chain infrastructure, enabling these solutions to be utilised at scale today.



Figure 1 Global refinery hydrogen plant age distribution (based on JM historic database)

### Valued assets

Fifty years ago, most of the hydrogen available on a refinery site was a by-product stream from the catalytic reformer. As clean fuel legislation progressed around the globe, SMR based hydrogen plants have been the means to produce the additional hydrogen needed to manufacture these clean fuels, providing ultra-low sulphur fuels that improve the environment in our cities and regions.

There are more than 700 refinery hydrogen plants around the world, and nearly 90% of these plants are SMR based. Over 40% are less than 20 years old, with many still being depreciated. These more modern plants have been designed to improve the efficiency and cost of the hydrogen produced, as well as manage the capital cost of the hydrogen plant.

For the last 30 years, most of these plants have been designed with pressure swing adsorption (PSA) based hydrogen purification systems that reduce the additional fossil fuel demand for the SMR through off-gas recycling. The plants' recycled stream, or PSA purge gas, is the predominant por- tion of the fuel to the SMR.

While there might be long-term refinery site or regional plans to introduce low carbon hydrogenfuelled energy through new blue or even green hydrogen assets to meet 2050 net-zero  $CO_2$  emissions targets, many existing hydrogen plants (see Figure 1) will be revamped to address the largest single source of  $CO_2$  emissions within the refinery.

### CO<sub>2</sub> in SMR based H<sub>2</sub> production

Conventional SMR technology comprises a fired heater with catalyst filled tubes, in which reforming reactions take place. Usually, gasified coal, natural gas, or other hydrocarbon based fuels, such as refinery off-gas and PSA purge gas, are burned with air in the fired heater to generate thermal energy required for the reforming reactions.

 $CO_2$  generated in the fuel side of the SMR is emitted in the flue gas stream and referred to as post-combustion  $CO_2$ . In general, the post-combustion flue gas is produced at low pressure and contains water, excess oxygen, and significant quantities of combustion related impurities from the fuel and air. Although technically complex, established solvent based technologies can be used to capture post-combustion  $CO_2$ .

The other source of  $CO_2$  originates from process-side syngas production, where natural gas is converted into a mixture primarily of  $H_2$ ,  $CO_2$ , and CO. This

syngas is processed in a WGS reactor to convert the bulk of the CO process stream (containing greater than 70%  $H_2$ ) into a PSA process to reach high level (99+%) purity  $H_2$  for use in hydroprocessing and isomerisation units to produce cleaner fuels.



The  $CO_2$  generated is at high pressure, and the process stream composition is simpler with minimal impurities, making it easier to utilise. Consequently, capturing this process-side byproduct  $CO_2$  is less complex and costly, and established solvent and absorbent based technologies can provide cost-effective solutions.



Figure 3 Minimising post-combustion  $CO_2$ : comparison of conventional to **ADVANCED REFORMING** technologies

### Capturing post-combustion CO<sub>2</sub>

In a post-combustion scheme,  $CO_2$  is removed from the flue gas stream. Amine based post-combustion technology has previously been deployed at a commercial scale, but uptake has been low due to high capture costs.4,5

New technologies, including amine based as well as cryogenic and other novel forms of post-combustion, focus on minimising cost and improving reliability. Using carbon capture at this location can achieve  $CO_2$  reductions of greater than 90%. However, since the SMR furnace operates at a negative pressure, the flue gas pressure is quite low and will complicate the design of the solvent based system.

Lower pressure requires larger equipment, needing more space. Plot space is likely at a premium at existing facilities. Fired heaters operate with excess O2, which will pass into the flue gas stream, while the make-up fuel will likely contain sulphur and other impurities. The amine solutions used for carbon capture are prone to oxidative and sulphur degradation.

Fresh amine will have to be added more often on a post-combustion system, increasing operating costs. There is also a significant amount of wastewater created by removing some impurities and reducing flue gas temperature.

### Capturing pre-combustion CO<sub>2</sub>

 $CO_2$  in the pre-combustion scheme is removed from the process stream after the WGS reactor and upstream of the PSA. The process stream will contain known components (H<sub>2</sub>O, CH4, CO, CO<sub>2</sub>, and N<sub>2</sub>), so impurities such as oxygen and sulphur are not present and will not contribute to the degradation of the amine solution.

Pressure control exists at the PSA inlet, meaning this stream will be available at high, defined pressure. These factors simplify the design and reduce the size of the removal system. In addition, the operating cost of the liquid amine based contact system will be lower for pre-combustion carbon capture.

While these systems benefit from smaller plot space (see Figure 2) and solvent stability, pre-combustion capture means only the process-side  $CO_2$  is removed. The total  $CO_2$  generated in a hydrogen plant can typically represent up to 60% of the total carbon emissions, but will vary depending on plant conditions.

### CO<sub>2</sub> capture efficiency<sup>2</sup>

Against this backdrop of conditions and challenges, there is a proven way to generate syngas at scale, in which all the  $CO_2$  comes out in a single stream at high pressure within the process, making it easy and economical to capture it with very high efficiency (i.e., 95% and above).

ADVANCED REFORMING technology, utilising heat exchange such as gas heated reforming (GHR) and other non-fossil fuel fired technologies, has been used at an industrial scale for decades and removes the need for a separate stream of methane fuel to be used to generate the tem- perature to drive the reactions.

	Process gas carbon capture	Flue gas carbon capture	Enhanced carbon capture
Maximum possible direct CO2 reductions	~50-60%	90%+	95%
Relative capital cost	45%	100%	70%
Relative plot space requirement	40%	100%	60%

### Post, pre, and enhanced carbon capture comparison, approximate values based on a study for a European refinery customer

#### Table 1

This in turn eliminates the dilute, low pressure outlet stream containing  $CO_2$  (post-combustion  $CO_2$ ) that results from the fossil fuel based firing. Some technologies generate heat with process-side combustion using oxygen or enriched air to drive the reforming reactions that generate the byproduct  $CO_2$ . This requires a source of oxygen, which is typically produced through air separation.

A GHR can be combined with an SMR or other **ADVANCED REFORMING** technologies for much greater heat integration, lower byproduct CO<sub>2</sub>, and lower carbon intensity than an SMR alone (see Figure 3). A GHR achieves this lower carbon intensity by using an SMR's hot outlet process gas or other **ADVANCED REFORMING** technology to heat the inlet feed gas to the GHR, enabling efficient use of natural gas within syngas production.

Enhanced carbon capture enables existing SMR hydrogen plants to achieve 95%+ CO<sub>2</sub> capture. As previously mentioned, existing SMR hydrogen plants are the single largest source of CO<sub>2</sub> emissions in the refinery. To futureproof existing SMR refinery hydrogen plants to align with 2050 net-zero targets, 90+% capture of the CO<sub>2</sub> emitted from the SMR hydrogen plant needs to be achieved.

Process  $CO_2$  capture in existing SMR based flow sheets does not get to this required level. While post-combustion  $CO_2$  capture can achieve this level of  $CO_2$  capture, it requires a high level of capital at a time when refinery capital is being compressed in response to the pandemic and capital utilisation is of greater importance.

In addition to cost, post-combustion capture requires a substantial plot plan to install (see Figure 2). As refineries continue to increase their complexity to make higher-value products, plot space is scarce and becomes more valuable, particularly for those refinery sites near metropolitan areas. However, the 90+% capture target can be exceeded by integrating **ADVANCED REFORMING** technology into existing SMR hydrogen plant flowsheets and producing hydrogen at a very low carbon intensity with improved heat integration. This integration moves the CO emissions predominately into the process side of the flowsheet, enabling low-cost CO<sub>2</sub> capture with minimal energy and plot space requirement (enhanced carbon capture). Table 1 shows a comparison of key parameters for these different decarbonisation approaches.

### Sustainability and longevity<sup>3</sup>

When looking at these bespoke decarbonisation solutions, consid- eration must also be given to the lifecycle emissions associated with implementing a new solution or technology. To utilise hydrogen in the future, energy infrastructure and electric grids need to be green. However, waiting for renewable energy to achieve a green electrical grid might be too late in some cases.

Therefore, using solutions that decarbonise outside the grid allows the end user to avoid competition for renewable energy with hard-to-abate sectors and allow significant carbon reductions to be achieved today. Applying integrated **ADVANCED REFORMING** technologies and enhanced carbon capture to existing refinery hydrogen plants provides a cost-effective way to achieve low carbon intensity hydrogen production today, sustained and aligned with green hydrogen production decades from now.

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