

Pre-combustion carbon capture

Pre-combustion carbon capture is the easiest route to rapid decarbonisation of the chemical and petrochemical sectors

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Through the years 2030 to 2050, it is inevitable that post-combustion carbon dioxide (CO₂) capture will be used to decarbonise heavy industry and fossil-fired power generation. Capturing CO₂ after air-fed combustion is expensive since the CO₂ concentration is low, and a huge volume of nitrogen gas must be processed.

Pre-combustion CO₂ capture has the benefit of operating at high pressure and often with a high CO₂ concentration. The consequence is that the combined Opex and Capex costs per tonne of CO₂ captured can be only 50% of post-combustion CO₂ capture. Retrofitting CO₂ capture to steam methane reformers (SMRs) for refinery hydrogen production represents a cost-effective way to achieve impactful decarbonisation.

Additionally, ammonia and ethylene oxide (EO) production must remove CO₂ from the process gases to ensure the chemical reactions and catalyst performance are effective. In these cases, the Capex and Opex costs of CO₂ capture are absorbed into the core process. These applications must represent some of the easiest routes to rapid decarbonisation of the chemical and petrochemical sectors.

Putting it into practice at Porthos

Air Products will retrofit a CO₂ capture facility at its existing Botlek SMR in Rotterdam. The SMR was built in 2011 with a capacity of around 100,000 tonnes of hydrogen per year. The annual CO₂ emissions at this production capacity would be more than 1,000,000 tonnes.

The retrofitted CO₂ capture, drying, and compression facility is expected to be on-stream in 2026. Retrofitting CO₂ capture equipment to an SMR of this size could cost in the order of €100 million. This represents an additional 50% of the original capital cost of the SMR. Steam

is required to operate the CO₂ capture facility, and power is needed to compress the dried pure CO₂. These represent the main operating costs.

Once operational, this will be the largest low-carbon or 'blue' hydrogen plant in Europe. The hydrogen from the Botlek SMR will continue to serve ExxonMobil's Rotterdam refinery and additional customers via Air Products' hydrogen pipeline and hydrogen liquefier.

ExxonMobil aims to achieve net-zero Scope 1 and 2 emissions from its operated assets by 2050. Since Air Products owns and operates the hydrogen production facility, the CO₂ emissions reduction is categorised as Scope 1 for Air Products and Scope 2 for ExxonMobil. This CO₂ capture retrofit with CO₂ sequestration in the Porthos scheme will allow Air Products to reduce its CO₂ emissions in the port of Rotterdam by more than half.

The Porthos CCS scheme is the first large-scale CO₂ transportation and storage infrastructure scheme in the Netherlands to achieve final investment decision (FID) and regulatory approval. CO₂ will be sequestered 3km beneath the surface of the North Sea in depleted gas fields, which lie about 20km from the coast.

When capturing CO₂ from an SMR, the location from which the CO₂ is captured influences the cost (see **Figure 1**). The lowest unit cost is to capture CO₂ from the pre-combustion syngas stream prior to the pressure swing adsorption (PSA) unit (Location A in Figure 1). At this point, the partial pressure of CO₂ is at its highest.

On the other hand, the maximum CO₂ recovery rate is capped at 70% because the post-combustion CO₂ from the SMR burners is not captured. To achieve low-carbon hydrogen certification in some markets, such as the EU, capturing CO₂ in the SMR flue gas may be

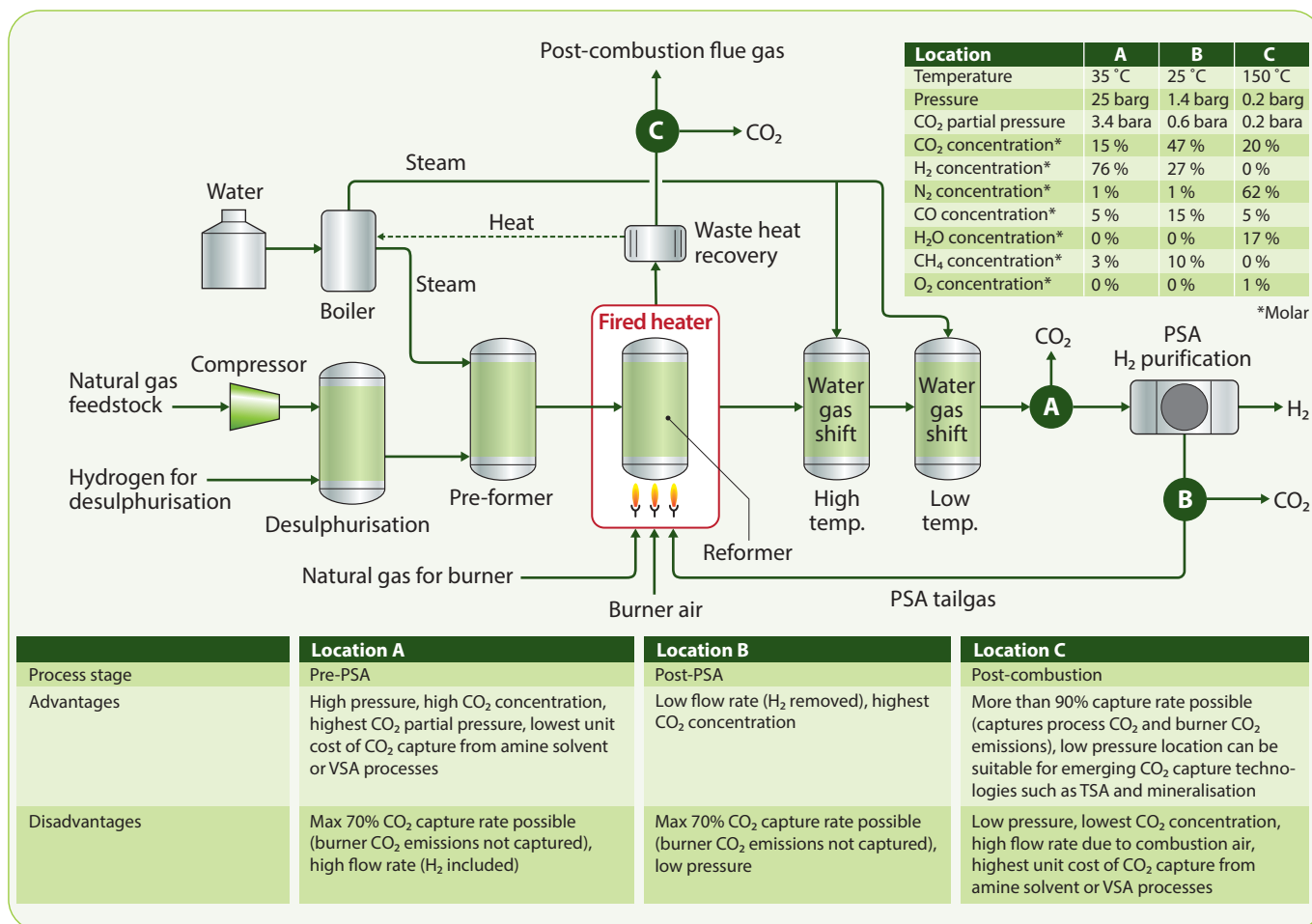


Figure 1 Potential locations for CO₂ capture from steam methane reforming

required to achieve the necessary CO₂ intensity of hydrogen production (Location C in Figure 1).

Low-carbon ammonia cracking and import

Blue ammonia may be produced at low cost in the US Gulf Coast, where natural gas prices are low and CO₂ storage can be achieved in locations close by, such as the Permian Basin. Linde and OCI will collaborate to produce 1,100,000 million tonnes per year of blue ammonia. Partial oxidation (POx) will be used to convert natural gas to syngas. The process operates at high pressure which reduces the pre-combustion CO₂ capture costs. CO₂ liberated during hydrogen production will be captured and sequestered.

The added cost for carbon capture and storage (CCS) is around \$120 per tonne of ammonia. This covers the additional equipment and energy costs to remove the CO₂ from the gas stream, transport it to a sequestration location, and inject it for permanent storage.

Many projects have proposed to produce green hydrogen at scale. The optimal locations are where there is abundant renewable power

generation potential from integrated wind and solar schemes, such as Western Australia. In the future, when electrolyser costs reduce and the efficiency of this technology improves, the cost of green hydrogen in these locations could potentially be comparable to blue hydrogen. Shipping and terminal infrastructure must be developed to connect the blue and green hydrogen producers with energy markets.

Air Products is also planning to make clean hydrogen available in Western Europe from cracked green or blue ammonia. The ammonia will be imported through the ports of Rotterdam and Hamburg. In Hamburg, Air Products will construct a new ammonia terminal for this purpose. At Rotterdam, Air Products has partnered with Gunvor to develop the import terminal. In Hamburg, Mabanafit will partner with Air Products.

In addition to the potential to crack ammonia to make hydrogen, low-carbon ammonia can be fired directly to generate steam in boilers or power on specially constructed gas turbines. On a smaller scale, it will also see application

as a maritime fuel and may also be used for industrial transportation applications in rail and trucking operations.

CO₂ capture is integral to ammonia production

In many large-scale ammonia plants, hydrogen is produced using a two-stage reforming process. The primary reformer is generally an SMR. The secondary reformer is an autothermal reformer (ATR), which requires oxygen for partial oxidation reactions. In this configuration, oxygen has traditionally been supplied by introducing air, as shown in **Figure 2**. The nitrogen that enters with the air remains in the process to be reacted with hydrogen in the ammonia synthesis loop.

Following the reformers, high-temperature shift and low-temperature shift reactors convert carbon monoxide (CO) and steam to hydrogen and CO₂. Subsequently, the CO₂ is removed using absorption and desorption in a solvent. The CO₂ must be removed from the gas stream prior to ammonia synthesis since any oxygen-containing molecules such as CO₂, CO, and water (H₂O) would poison the ammonia synthesis catalyst.

Hot potassium carbonate (HPC) is commonly used for this pre-combustion CO₂ capture application. After removing most of the CO₂ from the gas stream, there are drying and methanation stages. Methanation converts any residual CO and CO₂ to methane (CH₄) through a reaction with hydrogen, which is present in the gas mixture.

Leaving the methanation reactor, the gas is a mixture of nitrogen and hydrogen, with small amounts of methane and argon. Methane and argon are removed using a cryogenic nitrogen wash, such as the technology used in the KBR Purifier ammonia process. This purge gas can be burned in the SMR to yield heat for the reforming reactions.

The Burrup Fertilizers Ammonia Plant in Australia, now owned by Yara, was commissioned in April 2006. At that time, it was the largest implementation of the KBR Purifier process. The maximum ammonia production capacity is 2,600 tonnes per day (t/d). In 2019, EuroChem Group AG started up a new 2,890 t/d ammonia plant based on KBR's Purifier ammonia technology. The facility is the largest ammonia plant in Europe.

The CO₂ emissions from either the Burrup or EuroChem ammonia plant would be more than 2,000,000 tonnes per year (t/a). Since this CO₂ must be removed from the process to enable ammonia synthesis, there is no additional capital or operating cost associated with the CO capture aspect of CCS. With a small incremental investment in CO₂ drying and compression, CO₂ from ammonia facilities can be transported by pipeline to a suitable sequestration location.

Nitrogen and oxygen production for ammonia synthesis

An alternative pathway for ammonia synthesis is to react pure nitrogen and pure hydrogen

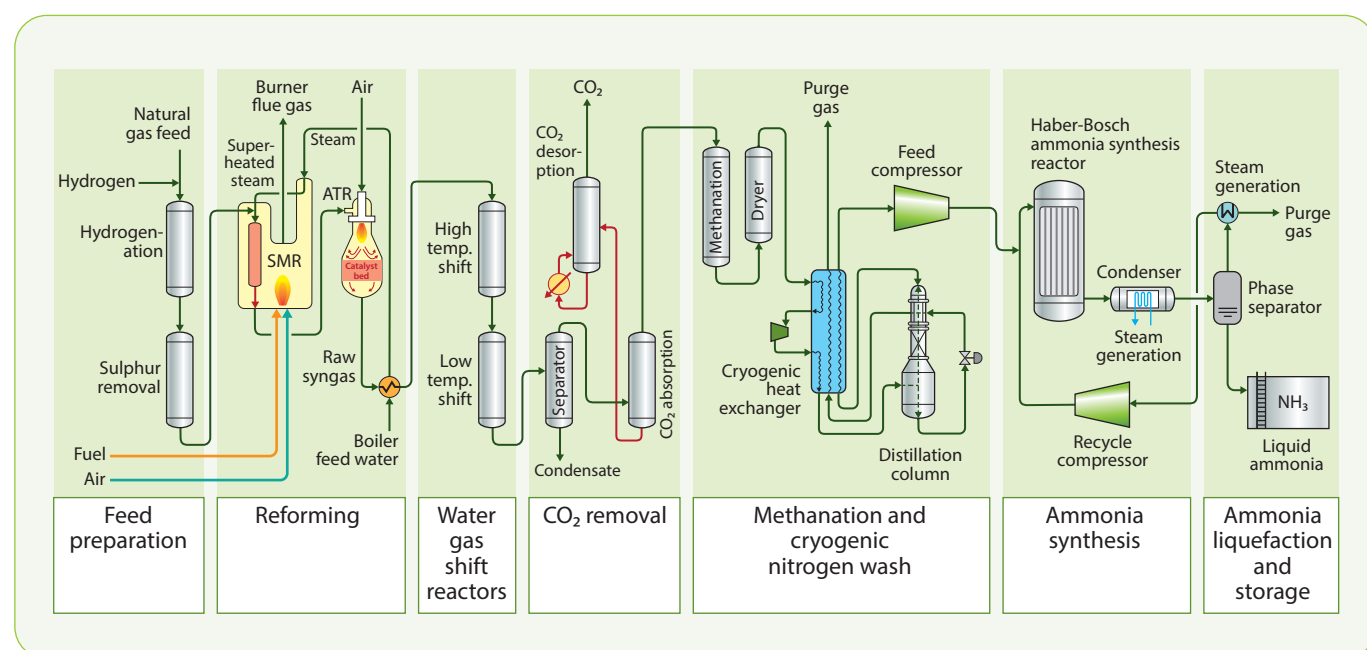


Figure 2 Air-fed ammonia production process

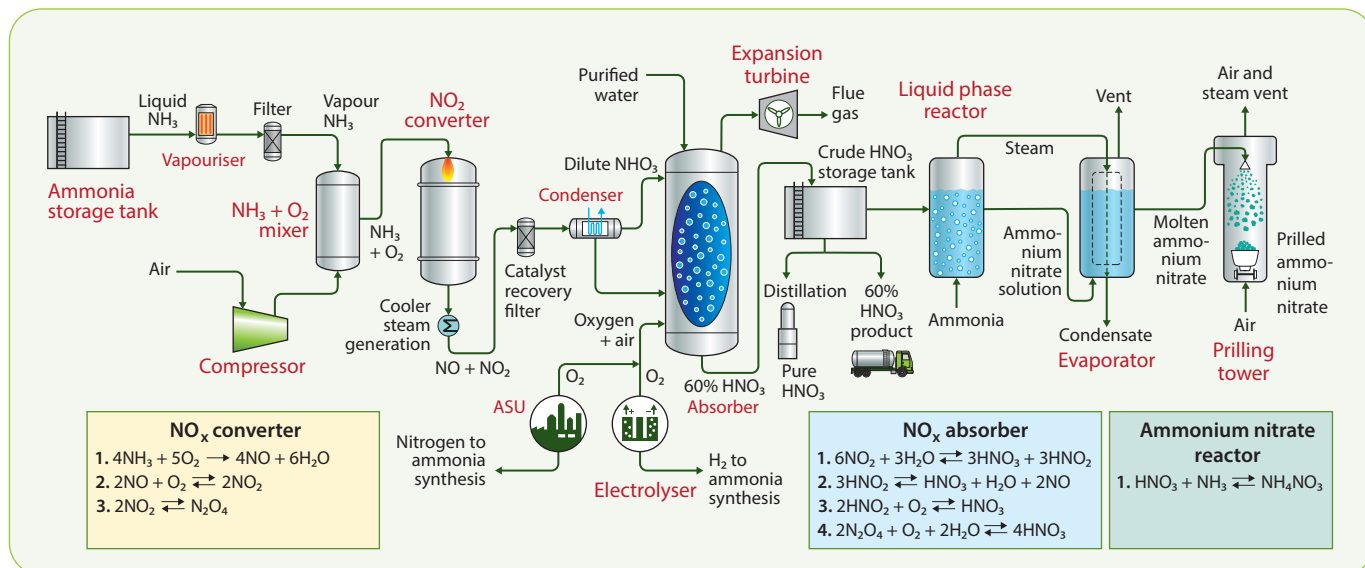


Figure 3 Nitric acid and ammonium nitrate production

together. In this pathway, hydrogen can be produced on a reformer with water gas shift reactors. After the reformer, hydrogen can be separated from unreacted methane, residual CO and CO₂ using a PSA system.

Nitrogen can be supplied to the ammonia synthesis process in a variety of ways, depending on the scale required. The ideal choice may be an on-site cryogenic nitrogen generator. It can provide a high volume of high-purity gaseous nitrogen to the ammonia synthesis process and may simultaneously produce liquid nitrogen, which can be stored in a cryogenic vessel on-site as a backup to the cryogenic nitrogen generator.

On the other hand, if pure oxygen is required for an ATR or POx reactor, a cryogenic air separation unit (ASU) may be appropriate. It removes argon from the nitrogen, reducing the requirement to purge argon from the ammonia synthesis loop. It also provides nitrogen for ammonia synthesis and oxygen to the reformer. Additionally, it can produce liquid nitrogen and oxygen for back-up storage.

Cryogenic nitrogen and oxygen production technologies use electricity as the main energy source. Decarbonisation can be facilitated by sourcing renewable power to run the process.

Nitric acid and ammonium nitrate

Nitric acid is produced by the Ostwald process. The first stage of this process is to oxidise ammonia to form nitric oxide. The gases from the reactor are passed into an absorber where oxygen is added to further oxidise the nitric

oxide to nitrogen dioxide, which is dissolved in the liquid to yield nitric acid at about 60% concentration.

Oxygen enrichment of the air feed to the absorber can achieve process intensification. In an integrated ammonia and nitric acid facility, an ASU can provide oxygen to the nitric acid process and nitrogen to the ammonia process. Alternatively, oxygen-enriched vent gas from a nitrogen generator, containing around 35% oxygen, can be used to feed the nitric acid absorption column.

In the future, it is possible that green hydrogen for ammonia production will be produced by the electrolysis of water. Oxygen is produced as a co-product during electrolysis. In such a scheme, the oxygen can be used to enrich the air stream to the absorber for nitric acid production.

Ammonium nitrate (AN) is produced by reacting nitric acid and ammonia (see **Figure 3**). AN is one of the main nitrogen-containing fertilisers used worldwide. It can be blended with fuel oil to create ammonium nitrate-fuel oil (ANFO), an explosive in the mining industry.

Parallels with ethylene oxide production

Around 20 million tonnes of EO are produced each year. The majority of this EO is converted to monoethylene glycol (MEG) and polyethylene glycol (PEG). The modern process to produce EO combines pure oxygen from an ASU with ethylene. The ethylene is generally produced on a steam cracker unit from crude oil or ethane, which is a component of many natural gas

streams. The reaction takes place at around 20 bar pressure and 250°C.

In the presence of a catalyst, oxygen reacts with ethylene to produce EO, and some CO₂ is also generated. However, the conversion rate of ethylene to EO over the catalyst is not very high, and a gas recycle is used to ensure high overall conversion rates.

CO₂ capture is essential in EO production to avoid an accumulation of CO₂ in the reactor gas recycle loop. This CO₂ must be captured and removed from the EO production process, and the associated capital and operating costs are absorbed in the EO production cost.

CO₂ capture in the ethylene oxide process

Gases leaving the EO reactor are generally at around 20 bar and contain around 4% oxygen and 8% CO₂. Hot potassium carbonate (HPC) is ideal for selectively removing CO₂ from high-pressure gas mixtures such as this. Unlike amine-based CO₂ capture solvents, HPC is not degraded by the oxygen present in this stream.

The equipment used to capture CO₂ is generally a twin-tower absorber and stripper system (see **Figure 4**). The gas leaving the CO₂ stripper

column is rich in CO₂, with water vapour being the main additional component. Much of the water vapour can be removed simply by cooling, followed by gas/liquid phase separation in a knock-out drum. This stream is ideal for feeding directly to a CO₂ liquefier or compressor and pipeline scheme for CO₂ transmission.

As carbon capture is an integral part of the EO production process, the incremental cost of CO₂ transportation for injection at a sequestration site or for utilisation is low in comparison to processes in which a post-combustion CCS scheme is required, with the consequential additional energy inputs to capture the CO₂ from the flue gas. To achieve rapid, cost-effective decarbonisation within the petrochemical sector, sequestration of captured CO₂ from EO production must be a priority.

Captured CO₂ utilisation

The Dow Chemical Company is the world's second largest producer of EO. At the Terneuzen chemicals complex in the Netherlands, Dow can produce up to 195,000 t/a of EO. Dow also produces the Meteor EO-Retro 2000 (MR2000) catalyst for EO production.

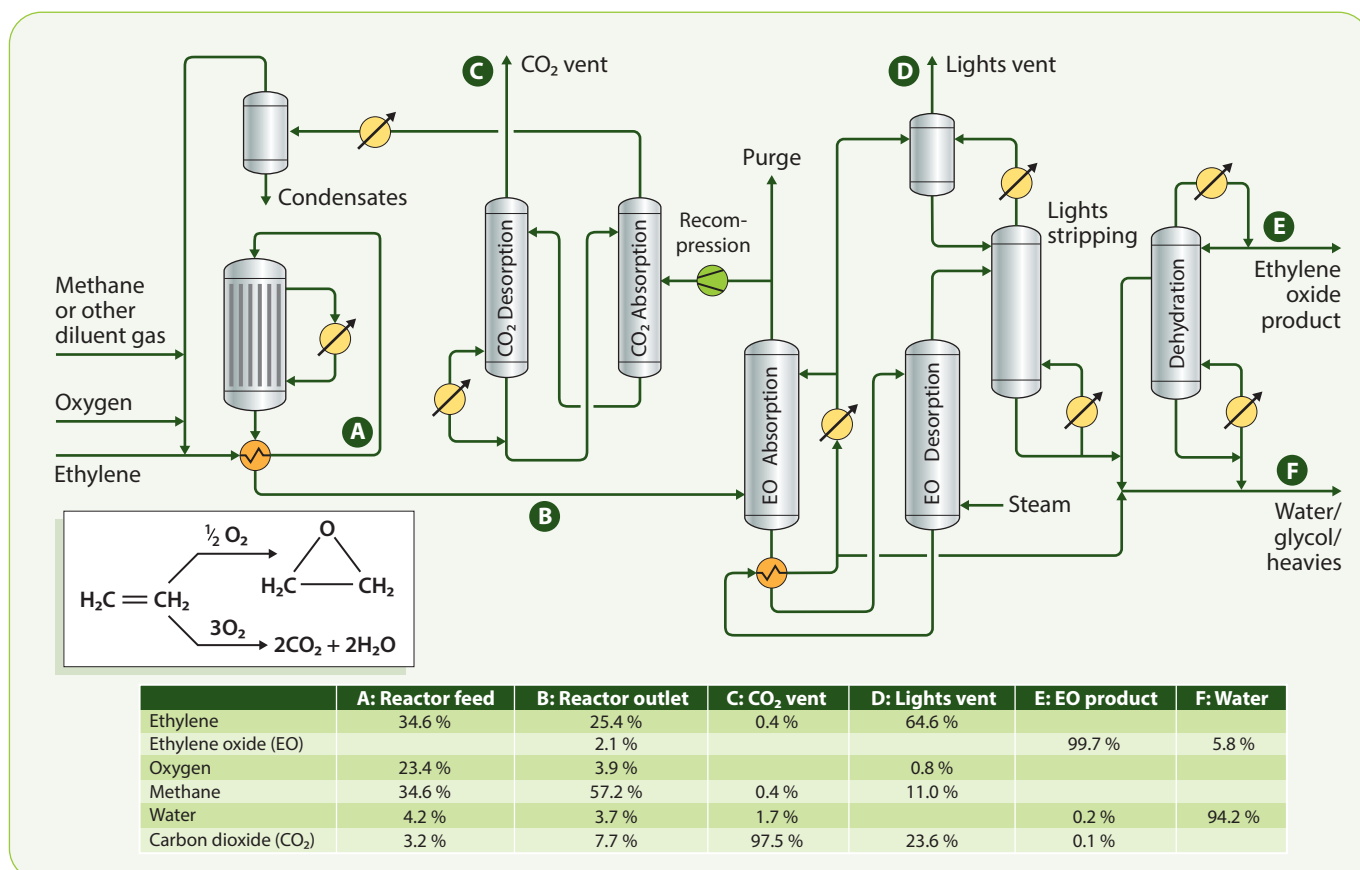


Figure 4 Oxygen-fed ethylene oxide production with integrated CO₂ capture

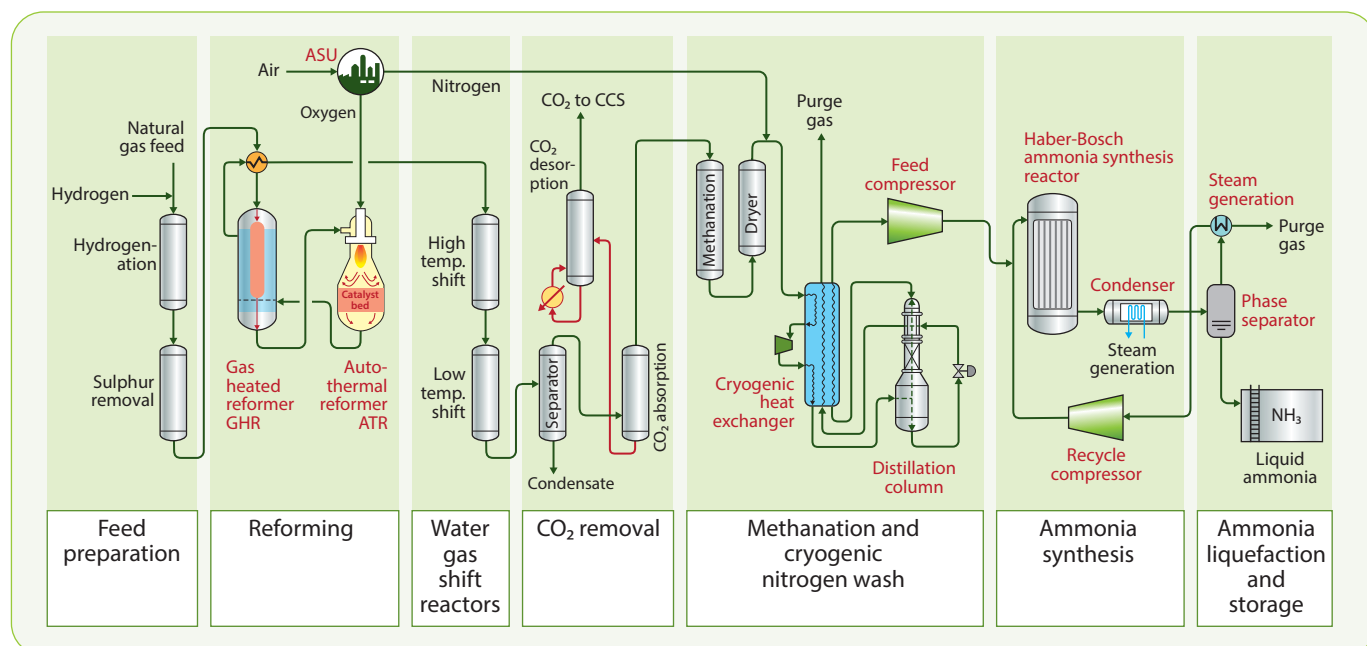


Figure 5 Blue ammonia production process with GHR/ATR

MR2000 was selected by MEGlobal Oyster Creek for its EO production facility, which started up in 2020. Linde operates an ASU to supply oxygen to the MEGlobal EO plant and recovers, purifies, and liquefies CO₂ captured from the EO process for distribution to commercial applications such as wastewater pH control, food freezing and beverage carbonation in the local market.

Gulf Cryo, a leading industrial gases company in the Gulf Cooperation Council (GCC) region, obtains CO₂ from one of Equate Petrochemical Company's ethylene glycol (EG) plants in Kuwait's Shuaiba Industrial Area. Equate is owned by The Dow Chemical Company and three Kuwaiti entities. A pipeline of several hundred metres transfers raw CO₂ from the stripper column on the EG plant to the Gulf Cryo site, where it is dried, liquefied, and purified using cryogenic distillation.

When Gulf Cryo's CO₂ capture and liquefaction process was commissioned in October 2014, it became the first CO₂ capture project in Kuwait with the capacity to liquefy 55,000 t/a CO₂. Sourcing this CO₂ as a byproduct from the EO facility avoids the use of a natural gas burner to generate CO₂ for local merchant applications, thereby minimising fossil fuel consumption and supporting decarbonisation.

Gas heated reforming

Gas heated reforming (GHR) was developed by ICI in the UK in the 1980s and referred to as the Leading Concept Methanol. Similarly, the Leading

Concept Ammonia uses a GHR for ammonia production. The GHR is followed by an ATR (see **Figure 5**).

Oxygen is injected into the ATR, where some exothermic partial oxidation reactions take place. The heat from these reactions maintains autothermal operation in the ATR and is also used to heat the GHR. Since the GHR is heated using syngas from the ATR, there is no need to have a fired burner in the SMR. This avoids the need for post-combustion CO₂ capture in this reforming configuration.

From 1994 to 2016, Coogee Energy operated a 70,000 t/a methanol facility at Laverton in Victoria, Australia. The plant used a GHR and ATR in the LCM configuration. Rising gas prices in Victoria rendered the Laverton plant uneconomic after 20 years of successful operation.

To capitalise on the potential for a lower cost natural gas feedstock, Coogee proposed a AU\$500 million investment in a 350,000 t/d methanol plant in Darwin Harbour, in Australia's Northern Territory. The potential for CCS in the Southeast Asia, north of Darwin, is high. Therefore, there would be good prospects for blue methanol production at this location using the GHR process and pre-combustion CO₂ capture.



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