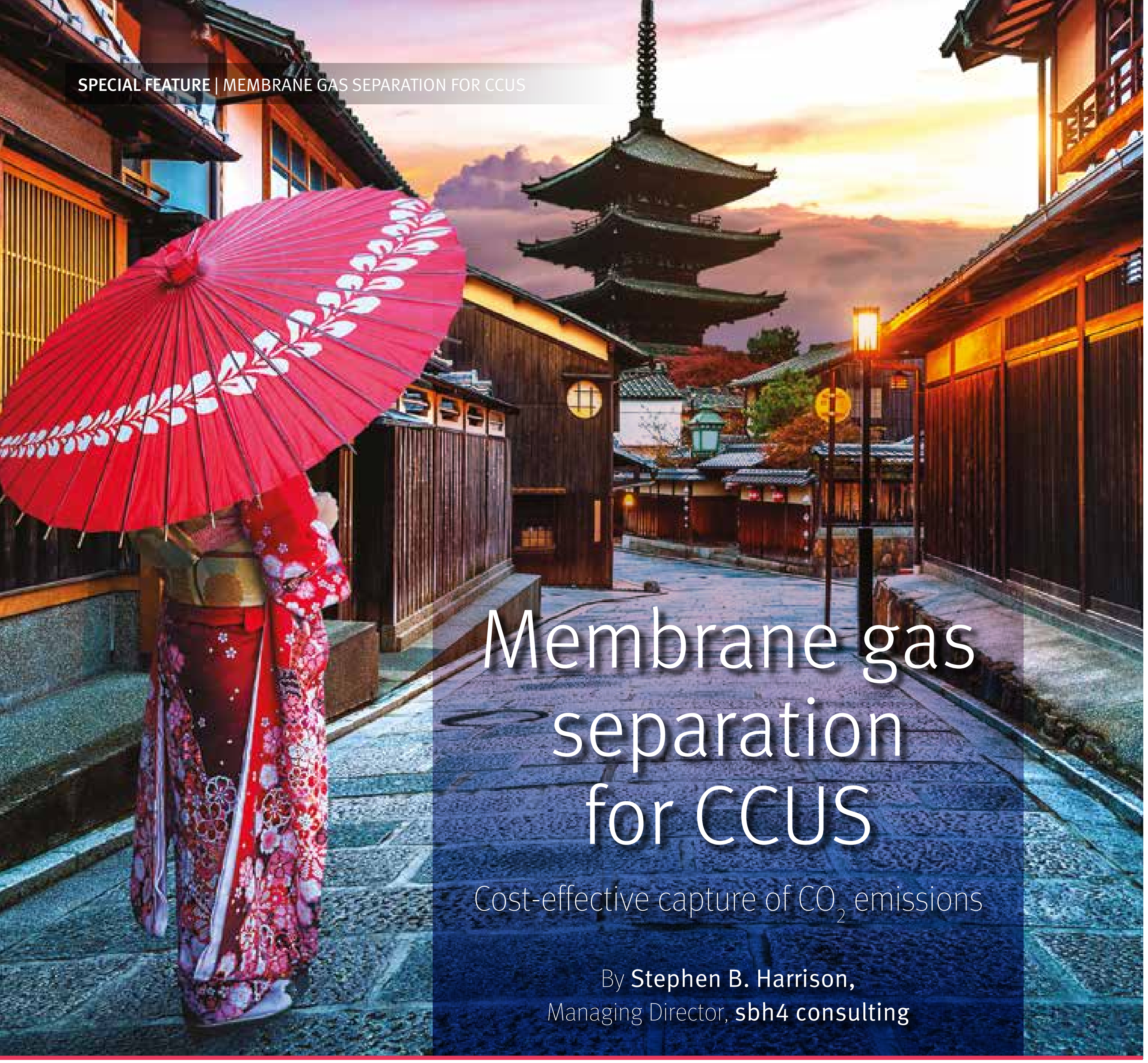

Membrane gas separation for CCUS

Cost-effective capture of CO_2 emissions

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Much of the CO_2 that enters the industrial gases value chain is captured from ammonia production. However, ammonia linked to fertiliser production can be seasonal and as the UK CO_2 shortage of June 2018 and the repeat episode in summer of 2021 have demonstrated, a diversified mix of CO_2 sources beyond fertiliser plants is more robust.

Biogenic CO_2 that is produced as a by-product of bioethanol fermentation is popular for food-grade applications. Biogas to biomethane upgrades are also increasingly being fitted with CO_2 capture and purification equipment. As environmental concerns increasingly drive purchasing decisions by industrial gas end-users, having access to sustainably sources biogenic CO_2 is seen as a source of competitive advantage in an increasingly competitive market for industrial gases suppliers.

In addition to these biogenic sources, CO_2 is increasingly being recovered from refinery SMRs due to their large scale and continuous operation. Having access to a secure all year-round source of CO_2 is a means to differentiate industrial gases supply through the promise of reliability and can result in significant competitive advantage.

Membranes for optimised CO_2 capture from refinery SMRs

Within the past decade, Air Products has implemented CO_2 capture from two steam methane reformers (SMRs) at the Valero refinery in Port Arthur in the US. The captured CO_2 from that process is compressed to above its triple point in an 8-stage intercooled centrifugal compressor. It is fed to a 21km CO_2 feeder pipeline which connects to a larger CO_2 transmission pipeline that runs 500km to oil fields in Texas and Louisiana where the captured CO_2 is used for Enhanced Oil Recovery (EOR).

As an alternative to PSA, the Air Liquide CRYOCAP™ process relies on membranes that operate at cryogenic temperatures to capture CO_2 from SMRs. A benefit of this proprietary technology is that the hydrogen yield from the reformer is increased in addition to achieving CO_2 capture. The increased hydrogen production can offset some of the costs of the CRYOCAP™ plant installation and improve the economics of the project.

CRYOCAP™ has successfully been implemented on a very large SMR operated by Air Liquide in France. The SMR supplies hydrogen to the Esso Refinery at Port-Jérôme on the banks of the river Seine. The captured CO_2 from that process is or further purified for commercial utilisation in a range of applications in food processing, beverages, and the manufacturing industry.

Air Liquide will also implement CRYOCAP at the Zeeland refinery, which is jointly operated by TotalEnergies and Lukoil in the Netherlands. The CO_2 from that plant is intended to be permanently stored under the Dutch North Sea in a CCS scheme.

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Gas fired power plant, Jakarta, Indonesia

In the future it is likely that the market for captured CO_2 in EOR or commercial applications will be saturated and decarbonisation through CCS will be the overwhelming motivation for carbon capture. In this context, there is very little prospect for revenue generation and cost minimisation will be key.

Energy-efficient CO_2 capture from flue gas emissions using membranes

In the coming decades, CCS will play a central role in decarbonisation. The main source of CO_2 emissions worldwide are thermal power stations fired by coal, gas, and fuel oil. As CO_2 emissions taxes are increasingly being applied around the world, CCS will become an economically viable technology that will play a vital role in the future CO_2-neutral energy and power generation system.

Experience has shown that 70-80% of the lifetime costs of a CCS scheme are related to CO_2 capture. The balancing 20-30% is related to CO_2 distribution to the sequestration site and the costs of developing the underground storage site and its ongoing monitoring. A major challenge facing these industrial sectors is therefore to achieve CO_2 capture at minimal cost.

Conventional carbon capture technologies absorb CO_2 into a solvent, such as an amine based chemical, or methanol in the RECTISOL® process. Alternatively, they can adsorb CO_2 onto a solid molecular sieve in temperature adsorption (TSA) process. In these cases, energy is required to subsequently separate the CO_2 from the solvent or the adsorbent. In the search for cost-effective technologies for carbon capture, utilisation and storage, membranes are being applied for carbon dioxide (CO_2) separation from flue gases.

The magic of membranes for gas separation

A benefit of using membranes for CO_2 capture in CCS schemes is that the CO_2 is not adsorbed onto a substrate or absorbed into a solvent, so it does not need to be separated again later in the process. This can help to reduce the energy and power consumption of CCS.

Whilst membranes are believed to be a high potential technology for CCS, they are not yet at a high technology maturity level. Technology development and scale up of membrane manufacture will be required to enable commercial application.

In the historic city of Kyoto in Japan, the university spin-out OOYOO is developing polymeric membranes. Their goal is to reduce the energy requirements to capture CO_2 from dilute industrial and power generation flue gases and enable cost effective CCS and support the fight against climate change.

In power generation the fuel is generally burned in air. Combustion flue gases therefore contain residual amounts of oxygen and a large amount ▶

© Bjoern Wylezich / Shutterstock.com | CO_2 transportation by ship, Nippon Gases

> "The perfect membrane for carbon capture will be able to withstand the high temperature of the flue gas and selectively remove the CO_2 from the background gas..."

of nitrogen from the air. Water vapour and CO_2 are the main gases produced during combustion. Pollutant gases such as carbon monoxide, sulpfur dioxide or nitric oxide are also produced during the combustion reactions.

Professor Easan Sivaniah is a leading technical advisor to OOYOO with many years of expertise in membrane technology for gas separation. Sivaniah says that, "the membrane we are developing has multiple layers that are built up like sheets of paper." Each layer is a polymer with a specific role. Some sheets provide structural strength and heat resistance; other films perform the gas separation through their highly selective mass transfer properties.

"A membrane operates like a sieve. Some gas molecules can pass through freely, whilst others are held back," adds Sivaniah. The perfect membrane for carbon capture will be able to withstand the high temperature of the flue gas and selectively remove the CO_2 from the background gas which is predominantly nitrogen. It must also be robust enough to withstand the presence of the pollutant gases, many of which can be corrosive – especially if heavy fuel oil, municipal solid waste, wood or coal are used as the fuel.

Cutting the cost of CCS

A major goal of CCS technology development is to reduce the cost of CO_2 separation from the flue gas. This is where polymer membranes have an advantage over ceramic membranes, which are very capital intensive.

Sivaniah states that, "OOYOO's target, is to achieve an energy requirement of 1.5 GJ or less per tonne of CO_2 captured from flue gas that has a relatively dilute CO_2 concentration of 10%." That is about half the energy requirement of current amine-based processes.

Sivaniah continues to explain that, "we are working to develop polymers that have good chemical properties and can also be produced at scale and low cost." The membrane must also have a low pressure drop because that influences the power requirements.

"The key is to have a highly selective and highly permeable, membrane that maximises the CO_2 throughput at minimal feed compression, whilst holding the other gases back."

The pioneering R&D work at OOYOO has attracted funding from various academic and governmental programmes. An essential next stage will be pilot scale demonstration of the technology in the field. This will require production of small batches of the membrane. When the process has been optimised at this scale, full-scale commercial production of the membrane polymer sheets, and the membrane modules will be required.

"We have successfully proven the viability of our membrane in our laboratory in Japan, within OOYOO's own modules," declares Sivaniah. "This is the first step in the journey to bring OOYOO membranes into range of technologies that will support decarbonisation worldwide."

Membranes for industrial gases applications beyond CCS

Cryogenic air separation can be tuned to produce high purity oxygen, nitrogen, and argon from the same plant. PSA and membrane systems operate to produce either oxygen or nitrogen at the required purity, but do not separate air into its main components.

Lasers that are used to cut metal can be fed with nitrogen which is generated onsite using membranes. Evonik's SEPURAN® membranes are ideal for such applications and have been integrated into gas supply equipment by Linde.

In the future, membranes could be used to separate hydrogen from methane. Hydrogen that has been admixed into the pipeline for cost-effective transmission or distribution must be purified at the outlet so that it can be used on applications that require very high purity hydrogen, such as fuel cell electric vehicles for emissions-free mobility. gw