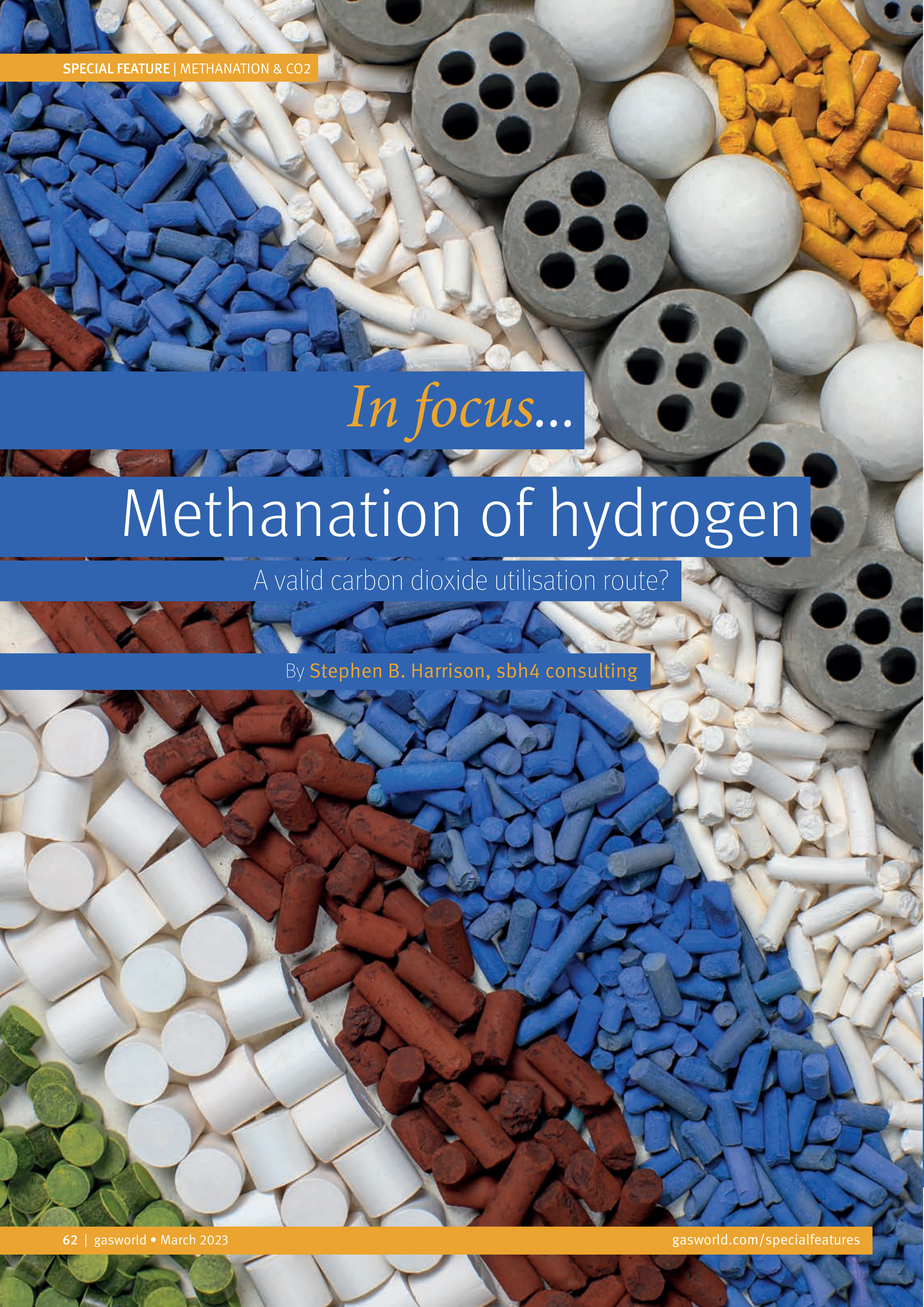

In focus...

Methanation of hydrogen

A valid carbon dioxide utilisation route?

By Stephen B. Harrison, sbh4 consulting

Methanation is the conversion of hydrogen and carbon dioxide (CO_2) to methane and water by the Sabatier reaction. It is essential in several chemical processes to remove residual CO_2 that may poison catalysts. Methanation has also been used to generate e-methane from green hydrogen. Is this a sustainable pathway to utilise CO_2 and generate a clean energy vector?

Most of the hydrogen produced today is derived from methane as natural gas. Coal gasification and electrolysis are also used to generate hydrogen but to a lesser extent. Given this situation, what motivation can there be to convert the hydrogen back to methane? After all, each chemical conversion results in energy losses so the more changes that are made before the energy vector is used, the less energy can usefully be recovered.

The motivation for methanation in ammonia production

More than 50% of the nitrogen applied as a fertiliser is through urea. Urea is an organic molecule and is sometimes referred to as carbamide. It has the formula $CO(NH_2)_2$. The production of urea is one of the most widespread and intensive CO_2 utilisation applications today.

Urea is formed through the reaction of CO_2 with ammonia. The ammonia is produced from hydrogen that is made on a steam methane reformer (SMR). During the reforming process, CO_2 is liberated. When released to the atmosphere that CO_2 is a greenhouse gas. In the urea production process, the CO_2 is captured from the SMR process gases to be utilised in the reaction with ammonia.

After syngas and hydrogen is produced in the SMR, the CO_2 is mostly captured to be utilised in the urea production stage. Then the resultant hydrogen it is fed to the ammonia synthesis reactor. However, the hydrogen stream is not pure, and it contains some residual CO_2 (around 0.3% by volume) and carbon monoxide (CO) at around 0.1%. These carbon oxides are poisons for the ammonia synthesis catalyst and their concentrations must be reduced to around only five parts-per-million (ppm).

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The mechanism to remove the CO_2 and CO from the ammonia synthesis feed gas is methanation. A nickel-based catalyst converts the CO_2 with a small proportion of the hydrogen in the synthesis gas to make CO and then reacts the CO with some additional hydrogen to form methane. The result is that the hydrogen concentration is reduced from around 75% to 74.5% and the methane concentration in the syngas increases from around 0.3% to 0.8%.

The small amount of methane that is fed to the ammonia synthesis loop builds up over time due to the recycling of gases around the loop. The methane is not reacted during this process so it must be purged with other inert gases because a high concentration of methane would damage the ammonia synthesis catalyst. The purge gas is predominantly hydrogen with around 10% methane. Nitrogen, argon, and ammonia are also present.

Flaring of the purge gas is possible, but wasteful. Separation of the hydrogen, nitrogen argon and methane is possible. The simplest form of purge gas processing is to remove the hydrogen using a selective membrane and allow the methane to flow to the SMR as fuel gas for the burners. Cryogenic techniques can enable the separation of gaseous

nitrogen and liquid argon from the purge gas. Nitrogen can be recycled to the ammonia synthesis loop or used as an inert utility gas on site. The argon is produced as a liquid, allowing commercial sale to local merchant markets.

Purification of white hydrogen

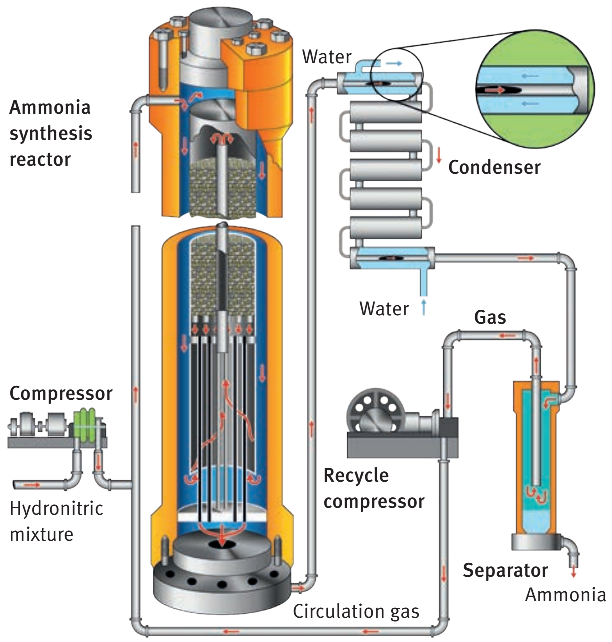
The rainbow of hydrogen colours is becoming well known. Green means renewable, blue means derived from natural gas with carbon capture and storage, turquoise is from methane pyrolysis. White hydrogen is the colour given to hydrogen produced as a by-product of industrial processes. Steam cracking of natural gas liquids is one of the dominant processes to produce ethylene. It results in the production of white hydrogen in addition to the target gas ethylene.

White hydrogen produced from steam cracking typically contains 500 to 5,000 ppm of CO. If the hydrogen is to be used in PEM fuel cells for mobility applications, this amount of CO would poison the palladium or platinum catalyst, so it must be reduced to less than 0.2 parts per million[1].

Methanation is the mechanism by which the CO can be converted to methane, which is not a poison to the fuel cell catalysts. Methane may exist hydrogen for PEM fuel cells used in cars and buses at a level of up to 100 ppm. If the methanation of CO results in methane levels exceeding 100 ppm, the hydrogen and methane can be separated using membrane or PSA technology.

Legacy concerns led to an interest in methanation of green hydrogen

Some years ago, the were concerns about blending hydrogen into natural gas transmission and distribution pipeline networks. These were driven by several factors such as the risk of embrittlement of steel pipelines that may cause



cracking and rupture. Metering and fair invoicing was also a concern. Regulatory hurdles were also in place that prevented high levels of admixing.

Research into hydrogen admixing into natural gas pipelines has been a major focus for transmission system operators (TSOs) and distribution system operators (DSOs) in the past decade. The conclusion that has clearly emerged is that hydrogen can indeed be safely blended into many natural gas pipeline systems under appropriate conditions. This finding has reduced the imperative to convert hydrogen to methane to enable its transportation to consumers.

Fair invoicing was also a concern. Natural gas metering

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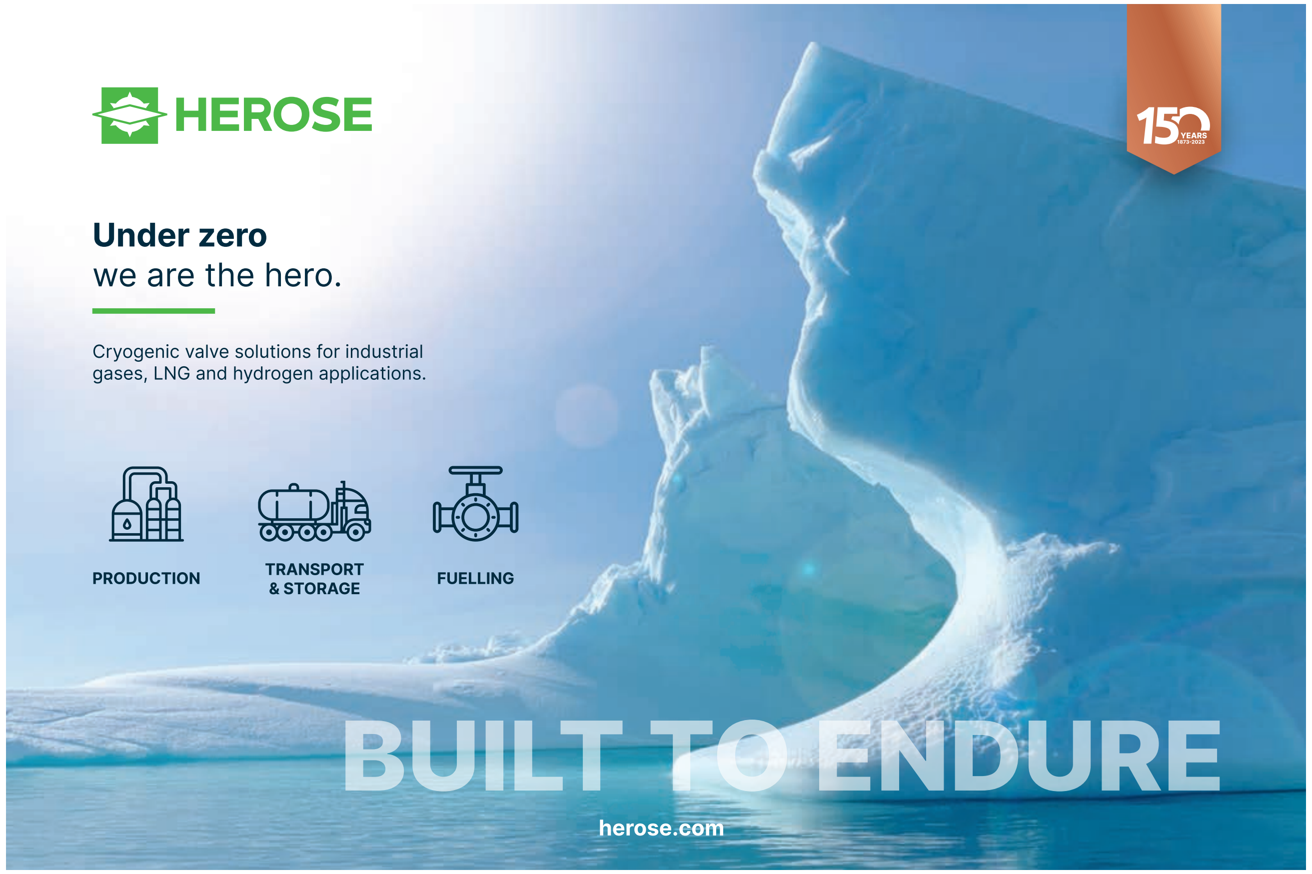

at the custody transfer point from the DSO to the consumer is done on a volumetric basis. Hydrogen has a slightly lower volumetric energy value than methane. This means that substituting methane for hydrogen results in the meter indicating that more energy has been delivered than is the case. It was perceived that changes in the metering equipment would have a prohibitive cost burden. Advances in metering technology for hydrogen/methane gas blends and an appreciation of the scale of mass-production that will be required has driven down the anticipated cost of switching out the metering equipment.

As an example, the technology firm Sensirion has developed an inline gas metering device that is able to measure any methane/hydrogen gas mixture. Its capability extends from pure hydrogen through to blends of hydrogen to biomethane and natural gas. Installing future-proof equipment such as this will avoid meter replacement as natural gas is gradually or fully substituted with hydrogen. Replacing a small fraction of the meters that exist in the gas distribution network would be much more expensive than installing multi-gas-capable meters today. So, planning ahead and using such devices now will make the energy transition more cost-effective for DSOs and consumers.

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The potential cost of changes in consumer equipment such as gas cookers or central heating boilers were also raised as a potential barrier to hydrogen blending into natural gas. Tests in this area have also established that up to 30% of hydrogen in the gas mixture by volume can flow through existing equipment without the need for modification. Since most systems are starting from a very low level of hydrogen blending, it will take some time until the 30% cap is reached. The concern that was raised has been robustly tested and suitable limits have been understood.

Green hydrogen is too precious to convert to e-methane

From a greenhouse gas (GHG) emissions perspective, an exclusive focus on 'decarbonisation' would drive a shift from fossil methane to e-methane generated from green hydrogen and recovered CO_2. However, climate scientists have accurately reminded us that methane, F-Gases, and nitrous oxide are also potent greenhouse gases and a holistic approach to GHG emissions reduction is required in addition to the foundation of decarbonisation. The implication here is that methane is a much more potent greenhouse gas than either CO_2 or hydrogen, so conversion of these comparatively benign greenhouse gases to methane results in the risk of gas leaks having a severely negative climate impact.

When green hydrogen is created, it is the equivalent of turning water into wine. The conversion of that premium 'champagne' energy vector into e-methane would seem to be an unnecessary additional step. It is wasteful in energy and increases the risk of methane GHG emissions and therefore poses an additional risk to climate change. gw

REFERENCE
1. ISO14687:2019, Section 5.1, Table 2, Grade D