Hydrogen sulfide A paradigm shift from waste to resource

Unlocking sour gas reserves for the hydrogen economy

By Stephen B. Harrison, sbh4 consulting

The natural gas price in mid-2020 was at an all-time low of $1.4/MMBtu. In the autumn of 2021, a four-fold increase to $6/MMBtu was observed as Asia built stocks in anticipation of a cold winter. In 2022, after Russia invaded Ukraine, prices are close to $9/MMBtu – six times higher than the low point two years prior.

LNG shipments from the Middle East and US to Europe and Asia are at an all-time high as Central Europe is switching gas supplies from Russia to other sources. Sustained LNG demand and high natural gas prices will ultimately stimulate investment in gas field development and LNG operations.

Unlocking stranded assets for additional LNG capacity

Sour natural gas reserves are tough to process, compared to sweeter gas. Projects such as ADNOC's Ghasha-mega project, where the gas contains 15% hydrogen sulfide (H_2S), have been difficult to justify due to the suppressed gas price.

At current gas prices, development of the Ghasha gas field would yield excellent returns. The same can be said for other sour oil and gas fields for which ADNOC has the concession, such as the Dalma zone, where H_2S concentrations in the natural gas are 5% and in 25% in the light crude condensate.

Gas can be used domestically in the United Arab Emirates (UAE) for power generation to increase energy autonomy and reduce the dependence on pipeline natural gas from Qatar. LNG can be exported to build currency reserves to fund investment in clean energy.

The Middle East is not the only place where sour gas reserves have been regarded as stranded assets. A small fraction of Canadian gas reserves contains more than 30% H_2S and more than half of Canada's gas reserves contain more than 2% H_2S. Upstream gas operators in Canada will take a fresh view of the economic viability of gas processing under the current pricing environment, combined with the prospects of strong and sustained LNG demand growth in Europe.

Sour gas: CO_2 and hydrogen sulfide

Sour gas is rich in carbon dioxide (CO_2) and H_2S. Sweet natural gas has low levels of these 'sour' compounds.

To enable gas distribution by pipeline, the H_2S must be removed to avoid corrosion of the gas transmission assets. If the gas is to be converted to LNG, then CO_2 must also be removed LNG to avoid blocking the liquefaction equipment with solid CO_2.

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CO_2 and H_2S removal are achieved using a double-tower absorption and stripping process in which an amine solution absorbs these sour gases. The process operates in the same way that CO_2 is cleaned from post-combustion flue gases in carbon capture and storage schemes.

Water is removed from the natural gas using a similar process, but glycol is the absorbent. Water must be removed to avoid corrosion of the gas pipeline ▶

Sulphur residue from gas processing

and avoid ice formation, if the gas is to be liquefied.

Elimination of H_2S emissions to the atmosphere has been mandated for decades to avoid the problem of acid rain. H_2S is generally removed after the amine treatment using the Claus process.

Residual H_2S or SO_2 tail emissions can be eliminated prior to the flue gas being released to air. The flue gas is rich in CO_2 and this stream is ideal for carbon capture and storage to reduce greenhouse gas (GHG) emissions. Rising CO_2 emissions taxation costs will see this additional process step being implemented in many locations.

Tried and tested: sulfur recovery with the Claus process

In the Claus plant, the mixture of CO_2 and H_2S leaving the amine treatment system is burned in air and H_2S is oxidised to SO_2. The SO_2 is then reacted with more H_2S over a catalyst to produce elemental sulfur. The Claus process is known to industrial gases experts due to the frequent use of oxygen enrichment in the burner for process intensification.

Many refineries have evolved their operations to process high-sulfur sour crude because low-sulfur sweet crudes are becoming rare and expensive. The result is that the refinery must recover more sulfur on the Claus plant that was originally sized to process sweet crude. Oxygen injection to the Claus plant burner can increase the sulfur removal capacity with minimal capital investment.

A paradigm shift: hydrogen sulfide as an energy resource

Refinery and gas processing Claus plants produce more than 50 million tonnes of sulfur each year. They account for most of the sulfur production worldwide.

Sulfur is used to vulcanise rubber during the production of tyres. It can also be processed to make sulfuric acid which has many applications in the chemical industry and is a feedstock to make the fertiliser ammonium sulfate.

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Despite there being some value for the recovered sulfur, H_2S removal has become a waste gas disposal problem. As the world begins to embrace hydrogen as an energy vector, the time has come to take a fresh look at H_2S: a molecule laden with hydrogen. Water (H_2O), also a hydrogen-loaded molecule, is processed in electrolysers to release hydrogen gas. Methane (CH_4), another hydrogen carrier, is reformed to release its hydrogen content. Using the right technology, H_2S can be split to yield solid sulfur and hydrogen.

Acid rain tree damage

Sulfuric acid storage

Splitting molecules with plasma and microwaves

Turquoise hydrogen is produced by splitting the methane molecule in a high energy, high temperature environment such as a plasma. The reaction takes place in the absence of oxygen and is referred to as methane pyrolysis. The carbon from the methane molecule is not released as CO_2, which is the case during reforming or combustion, but forms solid carbon powder.

Various plasma processes have been developed for methane pyrolysis. Monolith in the US has achieved a high maturity level with its Ocean Creek 1 plant in Nebraska. It will scale up production and build a new plant with the help of a $1bn loan from the US Department of Energy.

Plasma-based methane pyrolysis pilot plants have been built, or are under construction, by companies such as HiiROC in the UK, Plenesys in France, and Graforce in Germany. Some other technologies use molten metal, molten salt, catalysts, or microwaves to drive the methane pyrolysis process.

Plasma and microwaves can also be used to split the H_2S molecule. These technologies have also been demonstrated at pilot scale. Work at the Orenburg gas plant in Russia during the 1980s was conducted using 1 MW of power input to the plasma zone. About 10 years later, research at a refinery near Lviv in western Ukraine used a 50 kW microwave to produce 50m^3 per hour of hydrogen from H_2S.

These trials explored the relative economics of H_2S decomposition versus the Claus process. They could also generate hydrogen for use on the refinery for desulphurisation and hydrotreating of refined products. The Argonne National Laboratory in the US has also researched H_2S splitting with a view to improving the economics of sour gas processing.

Excellent economic potential

The Claus process requires very little energy input. Once the plant has been built and paid for, the operating costs are low. On the other hand, H_2S splitting with plasma or microwaves requires electrical power. The payback comes from the generation of hydrogen in addition to solid sulfur.

The thermodynamics of H_2S splitting, plus an allowance for balance of plant power requirements, requires circa 15 kWh / kg of hydrogen produced. With a nominal power cost of 10 cents per kWh (realistic in a gas-rich location with power generation on a gas turbine) the cost of hydrogen would be around $2/kg of hydrogen allowing for the power usage, capital depreciation, maintenance, and labour costs.

Based on recent natural gas prices in Europe, the cost of hydrogen from steam methane reforming is in the order of $4 per kg. This rises to $5 per kg if carbon capture and storage is implemented. The cost of green hydrogen production using electrolysis fed with renewable power is in a similar range.

H_2S splitting has the potential to be an economically viable pathway to hydrogen production. Furthermore, the sour gas reserve can be exploited to produce LNG or natural gas and the hydrogen revenue stream can diversify the revenue mix de-risk the investment, if LNG prices should fall in the future. gw

Sulfur residue in Canada