

Feedstocks and utilities for green hydrogen and e-fuels

High purity water, carbon dioxide and nitrogen are essential utilities for green hydrogen generation using electrolysis

Stephen B Harrison
sbh4 Consulting

For several years, attention has focused on green hydrogen as a clean energy vector. When produced on electrolyzers using renewable electrical power generated by wind, solar, or hydro schemes, green hydrogen has a very low carbon footprint. Ammonia is derived from hydrogen through reaction with nitrogen, sourced from air, in the Haber-Bosch process.

Many of the largest green hydrogen schemes proposed worldwide will convert green hydrogen to green ammonia for cost-effective shipping to international markets. Conversion of hydrogen to ammonia adds cost at the production location but means that ammonia, rather than hydrogen, can be shipped to the end-user destination.

Liquid hydrocarbon fuels are incredibly useful energy vectors due to their high energy density and ease of handling. As such, gasoline, diesel, aviation kerosene, and heavy fuel oil have become the fuels of choice for cars, trucks, planes, and shipping.

The challenge of the energy transition and decarbonisation is to substitute these refined products with sustainable, convenient, and cost-effective alternatives. Synthetic aviation fuel (SAF) is one such solution. SAF is a broad term meaning the fuel has been derived from non-fossil origins. The largest source of SAF today is biofuel, and more than 300,000 commercial flights operated by more than 40 airlines have used pure SAF or blends with fossil kerosene over the past five years. Thirteen major airports can refuel aircraft with SAF or SAF/kerosene blends.

Alternatively, SAF can be produced using renewable electrical power to make green

hydrogen or syngas for conversion to e-fuels through power to liquid (PtL) technology. In this pathway, carbon dioxide (CO₂) is required as the source of carbon to build the hydrocarbon molecules.

E-methanol burns with almost no emissions of particulates or sulphur dioxide. Methanol, like diesel and heavy fuel oil, does produce CO₂ emissions during combustion. However, since e-methanol is made from CO₂ captured from stack emissions or the air, its use is carbon neutral.

Whether the fuel is green hydrogen, green ammonia, e-methanol, or SAF, certification to identify the CO₂ intensity of the production process will be required as a guarantee of origin. In many markets, there are clear requirements emerging that the definitions of renewable fuels must move beyond simple 'grey' or 'green' labels to a more scientifically valid and environmentally robust classification system. Certification from an independent party to validate the product claims will inevitably be required.

Water, air, nitrogen, and CO₂ are the fundamental feedstocks to the above reaction pathways. Water and nitrogen also play key roles as utilities to enable safe and efficient operations (see **Figure 1**).

Crystal clear water: natural hydrogen carrier

Pure water supply to an electrolyser is essential. Electrolysis splits water molecules into oxygen and hydrogen. Supply of pure water to the electrolyser must be guaranteed. Failure to supply water means the electrolyser scheme must shut down. For a proton exchange

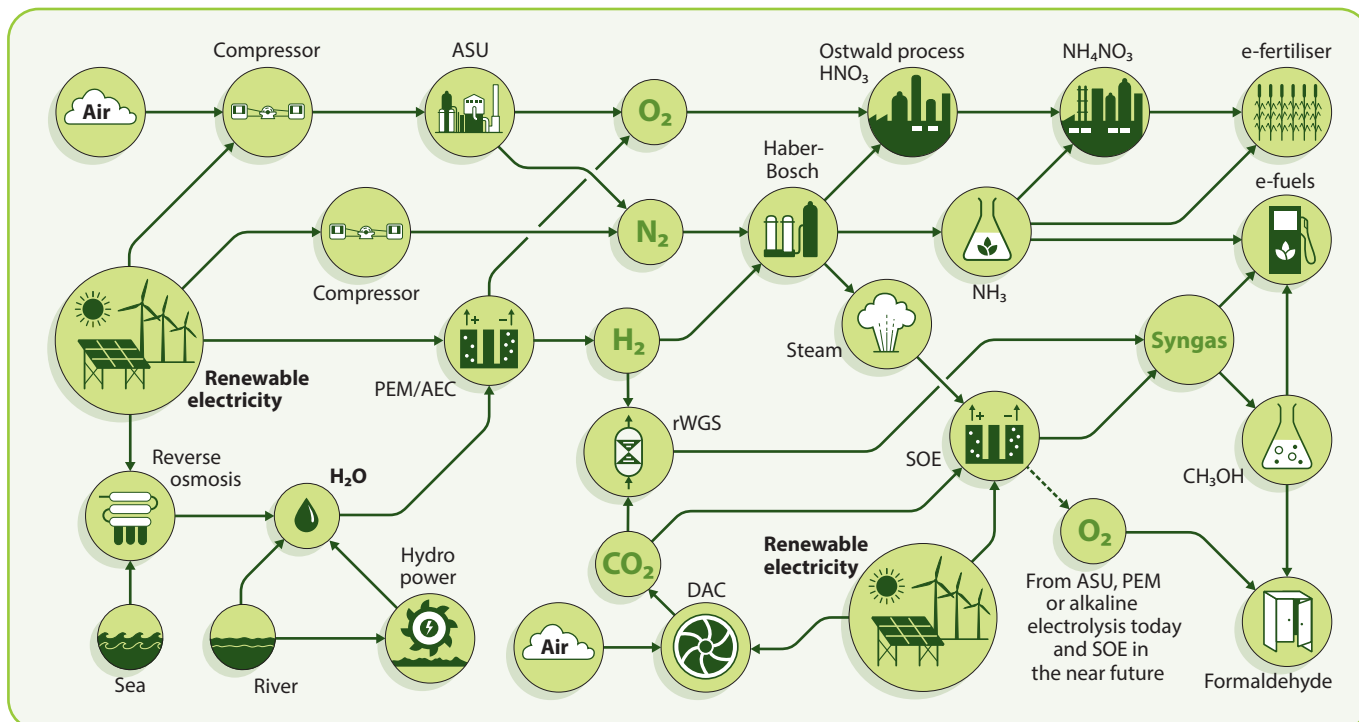


Figure 1 Air, water, and renewable electricity for integrated e-fuels, e-fertilisers, and e-chemicals production

membrane (PEM) system, that will probably not be a major issue, but for an alkaline system an unplanned shutdown may result in corrosion of the electrodes and a reduction in electrolysis efficiency during future operation (see **Figure 2**).

The capital and operating costs of pure water supply are low, but the costs of failure are high: reliability is key. Water supply for a typical green

hydrogen scheme will generally be only 1 or 2% of the total operating cost. Impurities such as calcium ions in the water will rapidly damage a PEM electrolyser membrane due to the interaction with the catalyst coating. Alkaline electrolyzers also have sensitivities to poisons in the water. The consequences of an impure water supply are unacceptable.

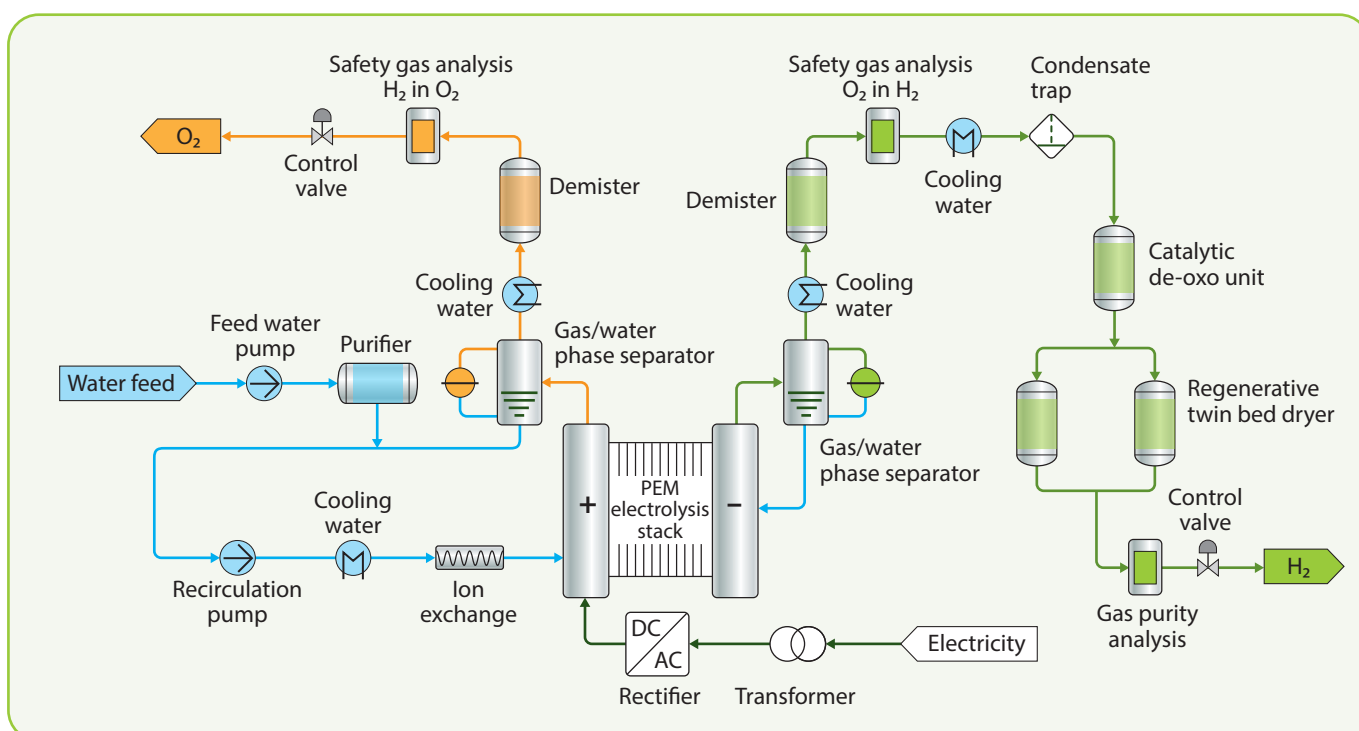


Figure 2 Pressurised PEM electrolysis process

The main quality parameter associated with the pure water supply to an electrolyser is conductivity. As a rule of thumb, a conductivity of less than 2 $\mu\text{S}/\text{cm}$ (0.2 mS/m) should be the target. Ions, such as calcium or sodium, that are dissolved in the water will increase conductivity. So, measurement of this parameter will confirm that damaging dissolved salts are not present. Electrolyser manufacturers will provide a more detailed specification for the feed water, and most will provide the necessary deionisation equipment as part of a complete package.

Purity standards for electrolyser feed water

Two internationally recognised standards refer to demineralised water purity for electrolysis. The US-based ASTM D1193-06(2018) Standard Specification for Reagent Water identifies three grades of purity. Many electrolyser producers will request supply of Type 2 water as a minimum purity. It has a maximum permissible conductivity of 1 $\mu\text{S}/\text{cm}$ (0.1 mS/m).

ISO 3696:1987 is an alternative to the ASTM document. It is titled 'Specifications for Water for Analytical Laboratory Use'. As with the ASTM document, the ISO Standard also includes three grades of purity, and the typical feed for an electrolyser would be Grade 2 with a maximum conductivity of 0.1 mS/m .

In addition to conductivity, the total organic content and total silica are important parameters for electrolysis feedwater. Maximum concentrations of these impurities are also specified in the above standards. Other contaminants to be avoided include carbonate and sulphate ions, as well as silicon and aluminium oxides.

Water desalination and purification

The main source of renewable power generation globally at present is hydropower. Where electrolysers are used in proximity to a hydro dam, there will always be access to fresh water to create hydrogen. However, the main ramp-up in renewable power generation is from wind and solar power. The optimum location for wind power generation is often offshore, in salt water. The best places to generate low-cost solar power are generally in arid desert locations with limited access to fresh water. Hence there will often be the need to desalinate water.

The technologies that will bring fresh water to electrolysis schemes are exactly those that are relied on today to make potable water available in arid locations. For example, thermal desalination is used extensively in the Middle East to make water available for the emerging vertical farming sector and coastal cities. Water tankers deliver fresh water to many villages in South Asia.

Inner Mongolia in China has vast solar and wind resources. The province's green hydrogen production target for 2025 is 500,000 tonnes. However, in this land-locked location, seawater desalination would be expensive and long pipelines would be required. The most cost-effective option here will be to drill deep for groundwater.

For use with electrolysis for green hydrogen, the default technology for seawater desalination and brackish water purification is reverse osmosis. This can be combined with some

In addition to conductivity, the total organic content and total silica are important parameters for electrolysis feedwater

thermal heat from solar radiation to avoid the use of fossil fuels. When used with freshwater, the reverse osmosis plant will operate at around 15 bar to generate water of electrolyser feedstock purity. For seawater desalination, a higher operating pressure of around 80 bar is used.

Pumping water to these pressures requires heavy-duty pumps with powerful motors. However, in the case of freshwater purification, the power required to operate the RO plant will be only 1 or 2% of the electrolyser scheme total. For seawater treatment, this may rise to 5%. If a solar-powered thermal desalination process is used upstream of the reverse osmosis plant, the water purification power requirement can be reduced.

To achieve the low levels of permissible conductivity of 0.1 mS/m , it may be required to use a polishing stage after the reverse osmosis plant. The most suitable technology for this is electro deionisation (EDI).

The water treatment plant can represent around 5% of the capital cost of an electrolyser

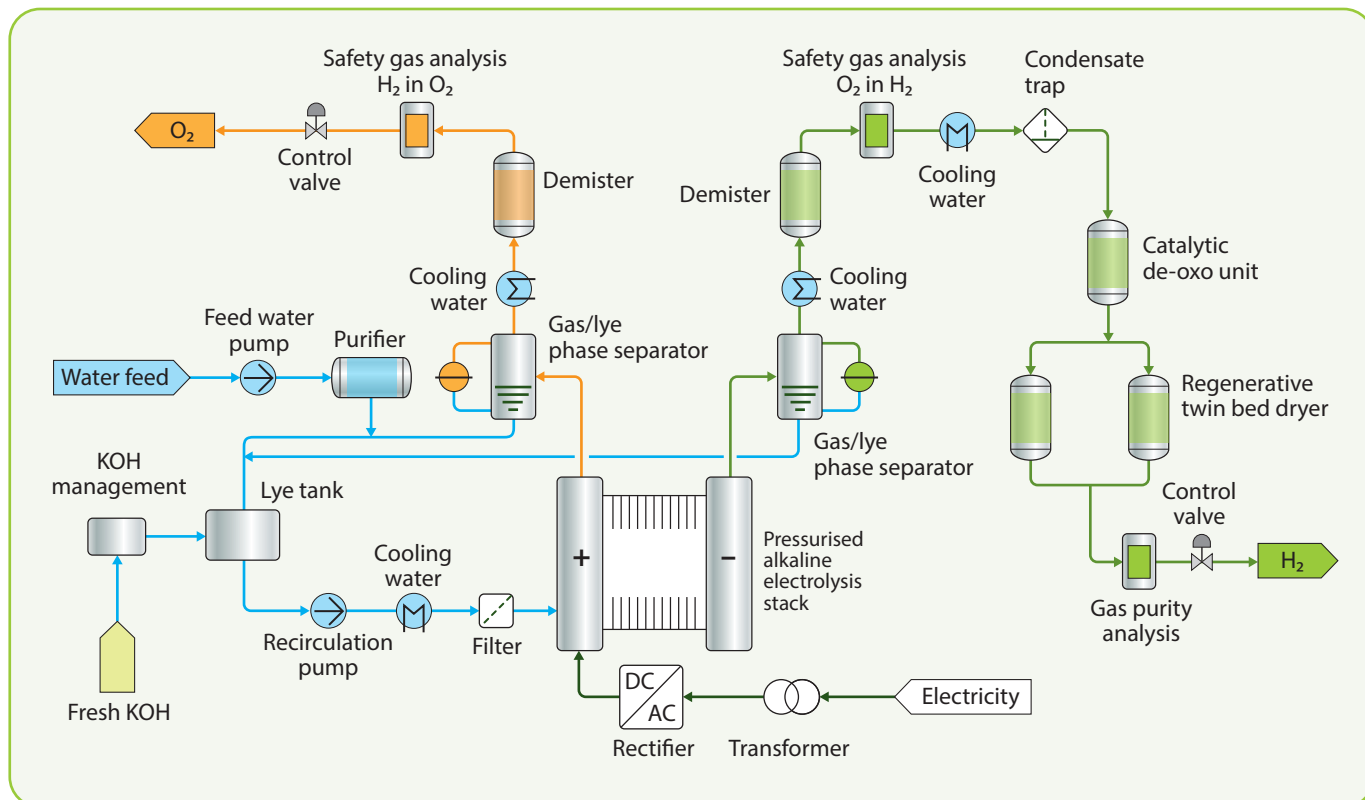


Figure 3 Pressurised alkaline electrolysis process

scheme. To put this into context, the power management system involving the transformer and rectifier to convert grid, wind, or hydropower to be suitable DC electricity for the electrolyser would be around 20%.

Cooling water and balance of plant power

Electrolysers are approximately 70% efficient when they convert power to hydrogen. The

wasted power generates heat which is generally dissipated on a cooling tower. A typical cooling tower will need about 2% of the daily recirculated cooling water volume to be topped up due to evaporation losses (see **Figure 3**).

The pumps that recirculate the cooling water, drive the cooling tower fans, and recirculate the electrolyte around alkaline electrolysers all consume power. However, the power demand

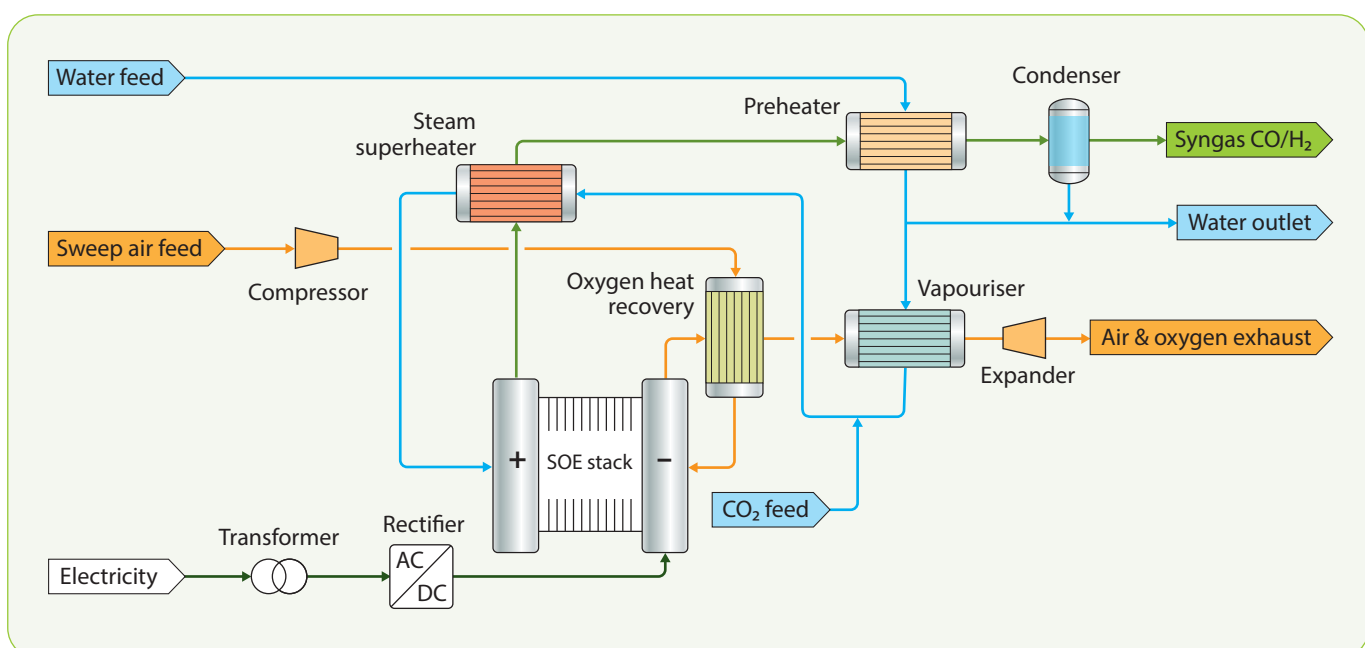


Figure 4 Solid oxide CO-electrolysis process for syngas generation

for these balance of plant items is only 10% of the total electricity consumption for an electrolyser system.

CO₂ feedstock purity for PtL and urea

A solid oxide electrolysis cell (SOEC), operating in co-electrolysis mode, consumes steam and CO₂ to yield syngas, which can produce e-methanol or liquid hydrocarbons through established chemical pathways, such as methanol synthesis and Fischer-Tropsch conversion. Introduction of steam to the SOEC means that water molecules are delivered to the electrolyser in a highly energised state. Therefore, about 25% less electrical power is required to split them than when using low-temperature electrolysis, such as a PEM or alkaline electrolyser (see **Figure 4**).

When e-fuels production is done in traditional refineries, waste heat or excess steam can often be fed to a SOEC. In stand-alone PtL processes for e-fuels production, exothermic reactions such as Fischer-Tropsch or methanol synthesis can provide the heat requirement of the SOEC. This integrated pathway results in high overall efficiency.

In co-electrolysis, both the steam and CO₂ must comply with the purity specification

required by the electrolyser. The requirement for CO₂ feedstock purification varies depending on its source. CO₂ captured from the combustion of fossil fuels can contain sulphur compounds that must be removed. The use of captured CO₂ reduces the overall CO₂ impact of SAF and introduces an element of circularity into the value chain.

CO₂ derived from direct air capture (DAC) is around three times more expensive than CO₂ captured from stack emissions. However, it is generally free of any potentially harmful impurities, and the purification costs can be avoided.

If no waste heat is available, it may be preferable to use an alkaline electrolyser to generate hydrogen. The hydrogen from an alkaline electrolyser can be reacted with captured CO₂ to yield syngas through the reverse water gas shift reaction.

In addition to CO₂ being a feedstock for e-fuels, it is required for green urea production. Urea is used to make fertilisers and resins and is formed by reacting CO₂ with ammonia. Thousands of tonnes per year of captured CO₂ could be utilised in this circular way to build carbon-neutral e-fuels, fertiliser and chemical molecules.

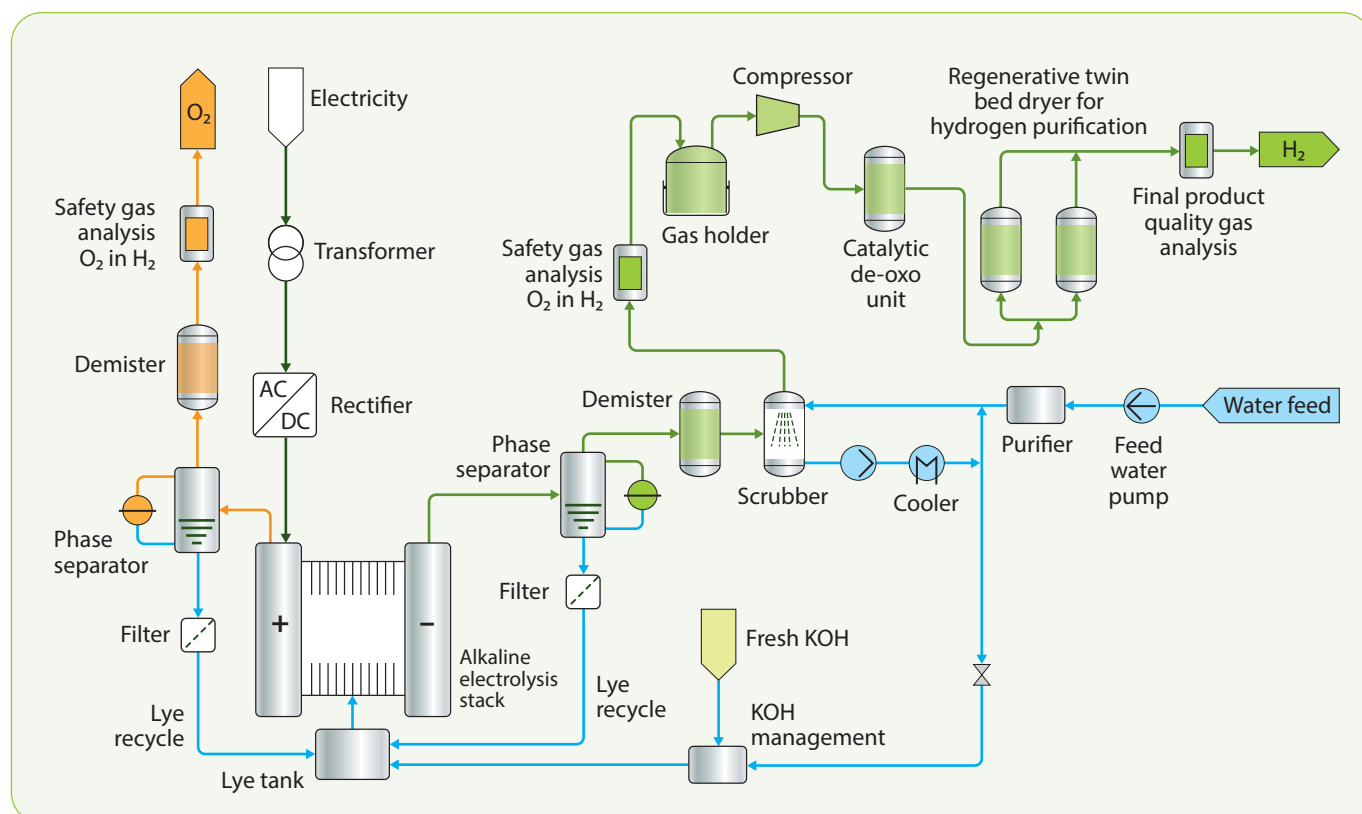


Figure 5 Low-pressure alkaline water electrolysis process

Nitrogen for safe electrolyser operations

The lower flammable limit (LFL) of hydrogen in pure oxygen at atmospheric pressure and 20°C is 4%. However, electrolyzers generally operate at 80°C; at this temperature the LFL reduces to 3.8%. Pressurised alkaline and PEM electrolyzers operate at between 15 and 30 bar. At 20 bar and 20°C, the LFL of hydrogen in oxygen increases to 5%. Both the operating pressure and temperature influence the flammability limit of hydrogen in pure oxygen (see **Figure 5**).

Electrolysis splits water to create oxygen in addition to hydrogen. In the PEM and anion exchange membrane (AEM) electrolyser types, these two gases are separated by a membrane. In pressurised and low-pressure alkaline electrolyzers, both gases are present together, dissolved in the lye electrolyte that circulates around the electrolyser.

During operation with variable renewable power, as the electrolyser ramps down with reduced power availability, the oxygen concentration in the hydrogen gas increases. Safety management systems in the electrolyser prevent the hydrogen concentration in the oxygen from rising to a dangerous level. When activated, these safety systems flood the electrolyser with inert nitrogen gas.

For a GW-scale green hydrogen alkaline electrolyser system working with a variable or intermittent renewable power source, there

could be several occasions per year where the system may need to shut down and initiate a nitrogen purge. At GW-scale operation, the amount of nitrogen required in these events may justify an on-site nitrogen generator.

Nitrogen generators use a cryogenic process that is a simplified version of a full air separation unit (ASU). Unlike the ASU, nitrogen generators are not designed to produce oxygen and argon as co-products. The focus on nitrogen reduces the specific power requirement, simplifies operation, and reduces the plant capital cost compared to an equivalent nitrogen flow derived from the more complex ASU.

Nitrogen feedstock for green ammonia

Ammonia is readily liquefied and, in this state, has a volumetric energy density 50% higher than liquid hydrogen. The reduced shipping costs of liquid ammonia, compared to liquid hydrogen, mean that Capex and Opex savings from shipping can be directed to the ammonia conversion facility. For long distances, such as the Australia to Europe route, liquid ammonia is the most cost-effective mode of green hydrogen transportation (see **Figure 6**).

One of the attractions of using ammonia as a fungible energy vector is that it is already a globally produced and traded commodity. Worldwide grey ammonia production is typically 185 million t/y.

The global merchant market for traded grey

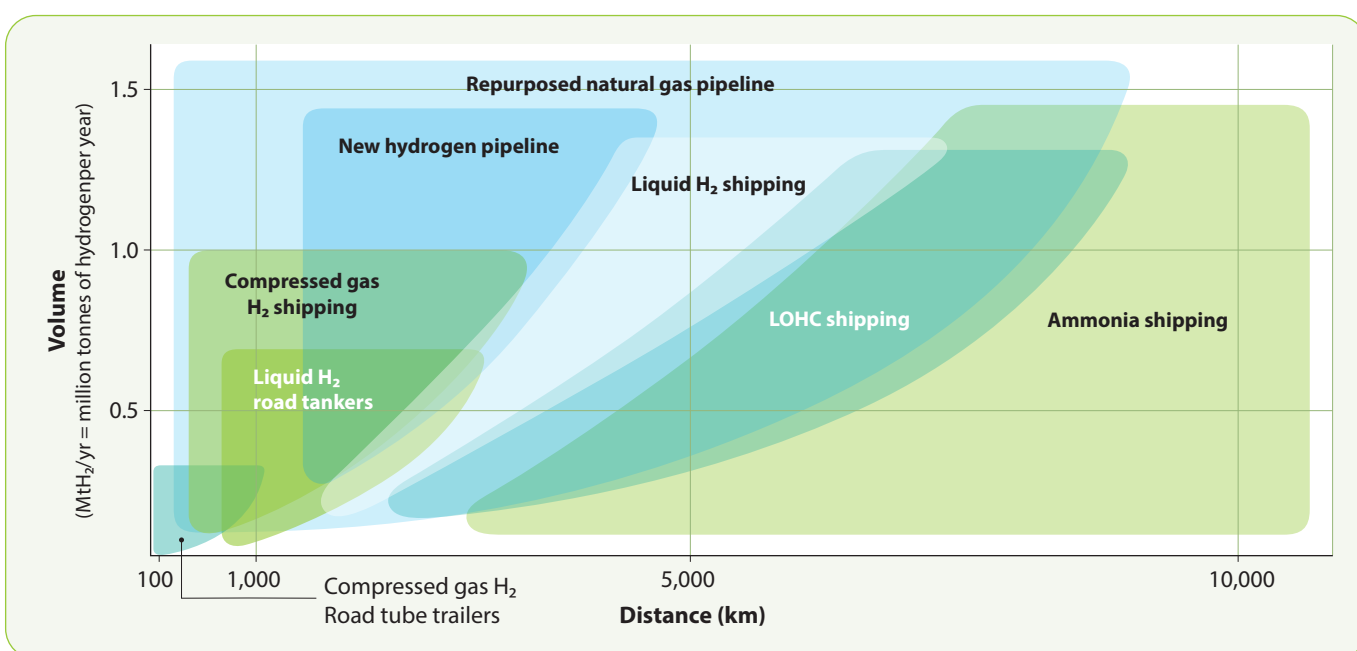


Figure 6 Hydrogen transport options when considering volume and distance

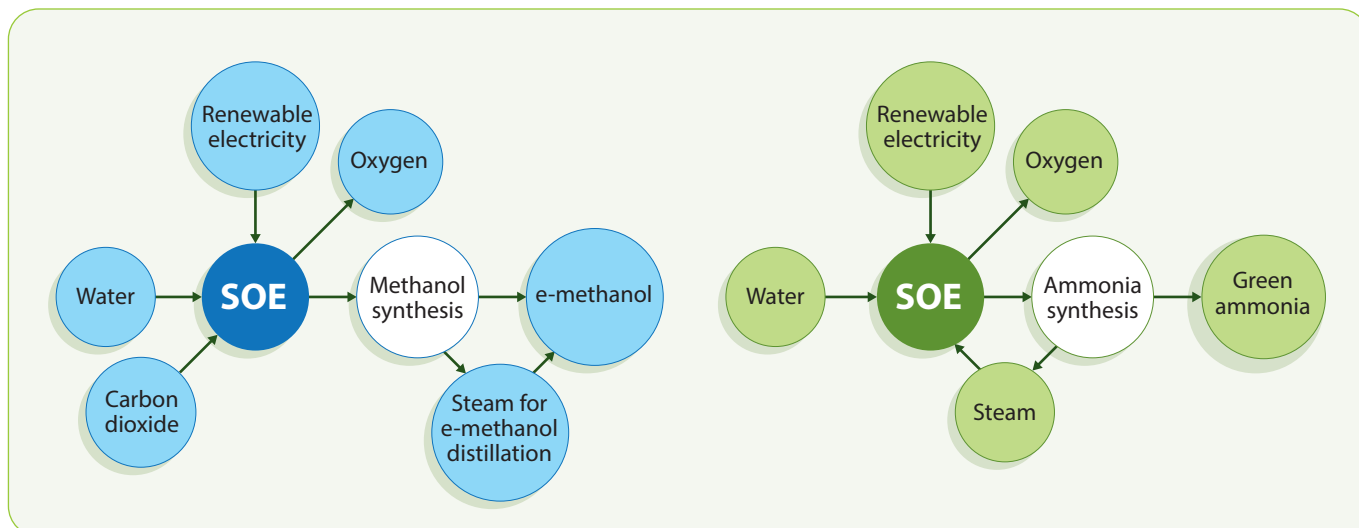


Figure 7 Solid oxide electrolysis for energy-efficient e-fuels production

ammonia, at circa 20 million t/y, represents about 11% of worldwide production. One hundred seventy ammonia tankers sail the world's oceans shipping these merchant ammonia volumes across 120 portside ammonia terminals. A typical ammonia tanker can transport 60,000 tonnes of liquid ammonia, and the terminal would typically be built to store twice this capacity. The maturity of the ammonia transportation infrastructure is an attractive reason for the use of green ammonia as a traded energy vector.

Merchant grey ammonia pricing is influenced by natural gas costs and supply vs demand balance. Significant underutilised ammonia production capacity exists in China. However, this is land-locked inland production and is not available to international markets, so utilisation of internationally tradeable ammonia capacity has been high. The pricing volatility of grey hydrogen and the lack of availability of excess capacity for international trade are key drivers for the development of new green ammonia capacity to supplement existing grey ammonia production.

Traditionally, ammonia plants have introduced air to the ammonia synthesis loop to bring in the required nitrogen. Using pure nitrogen instead of air means no oxygen is circulating in the ammonia synthesis loop. This minimises energy losses and reduces the required plant size, resulting in Opex and Capex reductions. In recent years, small to medium ammonia plants have tended to use a pure nitrogen feed from an on-site nitrogen generator.

The inputs required to operate a nitrogen generator are electrical power, cooling water, and ambient air. Using renewable electricity, the operation of a nitrogen generator can be fully sustainable. For the future generation of green ammonia projects, nitrogen generators will be ideal for supplying the required green nitrogen to react with green hydrogen to produce green ammonia.

Solid oxide electrolysis for Haber-Bosch process integration

Green electrons are highly valuable and result from significant infrastructure investment in wind and solar parks or hydro dams. Using them to produce green ammonia is essential to optimising project economics and reducing the cost of the energy transition. Using a solid oxide electrolyser or SOEC is highly efficient if hydrogen is to be converted to green ammonia (see **Figure 7**).

Steam generated by the Haber-Bosch ammonia synthesis reactor can supply up to 70% of the steam required for solid oxide electrolysis. Methanol synthesis is also exothermic. However, the heat liberated by the reaction of syngas to form methanol is generally used to purify the methanol using distillation. Therefore, alkaline, PEM or SOEC electrolysis technologies can be equally efficient for methanol production.



Stephen B. Harrison
sbh@sbh4.de