© Harald Pettersen | The Equinor Tjeldbergodden Grey Methanol Plant, in Norway

e-methanol, SAF and PtL

The future of CO_2 utilisation

By Stephen B. Harrison, sbh4 consulting

The route to decarbonisation and the energy transition has sometimes been described as defossilisation. Liquid fuels are incredibly useful energy vectors due to their high energy density and ease of handling. Gasoline, diesel, aviation kerosene and heavy fuel oil have become the fuels of choice for cars, trucks, planes, and shipping.

The challenge is to substitute these refined products that are derived from crude oil with sustainable, convenient and cost-effective alternatives.

Liquid fuels of a non-fossil origin are one such solution. They can be bio-based fuels such as processed waste frying oil. Alternatively, they can be produced using renewable electrical power to produce so-called e-fuels through Power-to-Liquid (PtL) technology. Thousands of tonnes per year of CO_2 (carbon dioxide) could be utilised in this way to build the required hydrocarbon molecules.

Methanol as a diesel substitute

Diesel has been the default fuel for trucks and buses for decades. Similarly, heavy fuel oil has been the maritime fuel of choice. Emissions of sulfur dioxide and oxides of nitrogen from these fuels have been progressively reduced through tightening environmental legislation. Each of these fuels produces sooty particles when burned in internal combustion engines.

e-methanol, on the other hand, burns with almost no particulate emissions and since it contains no sulfur, the emissions are free of sulfur dioxide. The use of e-methanol for road and maritime applications would reduce pollutant gas emissions. Methanol, like diesel and heavy fuel oil, does produce CO_2 emissions during combustion. However, since e-methanol is made from captured CO_2 the emissions are carbon neutral: e-methanol is not a fossil fuel.

Diesel can begin to freeze at around -10°C to -15°C; heavy fuel oil must be heated to ensure that it remains pourable. Methanol exhibits much better low temperature pour properties than diesel and heavy fuel oil and it remains usable in harsh winter conditions at -40°C. It is therefore an ideal fuel for use on trucks operating all year round in northern Europe and Canada, or for emerging arctic shipping routes.

As maritime fuels...

The environmental credentials of e-methanol are clear. Ammonia can offer additional benefits but comes with a safety warning. Whilst both methanol and ammonia are toxic, ammonia is significantly more so.

The Occupational Safety and Health Administration (OSHA) in the USA has set an eight-hour time weighted average of 50 ppm (parts-per-million) as the permissible exposure limit for ammonia. Methanol has a much higher permissible exposure limit of 200 ppm (OSHA) indicating that it is regarded as being less hazardous than ammonia. For ferries where many passengers are present on-board the ship and the boat will be present in ports with high population density, methanol would have a clear safety benefit versus ammonia.

Beyond the environmental impact, methanol is around 20% more expensive to produce than ammonia for the equivalent energy value. On the other hand, liquid methanol has a volumetric energy density of 15.7 MJ/L whereas ammonia lags by around 20% with 12.7 MJ/L. The implication is that circa 20% larger storage tanks or ships are required in the liquid ammonia supply chain, compared to methanol.

There are 120 grey ammonia terminals around the world, but they are aligned to chemicals and fertiliser production. These ammonia terminals are not ideally located for bunkering operations. Furthermore, there are no established ammonia bunkering services in major ports.

Grey methanol is produced at about 100 plants worldwide, with an annual capacity of around 140 million tonnes. Around 100 ports worldwide have methanol storage. Bunkering facilities have been implemented at some of these locations. Despite the existence of some methanol and ammonia bunkering facilities, extensive use of green ammonia or e-methanol as maritime fuels would require a significant ramp up in bunkering infrastructure.

E-methanol using captured CO_2 will be produced in the HyNL project in Eemshaven, northeast Netherlands. 200 MW of renewable power will be generated from offshore wind turbines in the North Sea. Much of that electricity will flow to a bank of 100 MW of electrolysers operated by Engie. CO_2 will be captured from the flue gas of the local waste to energy plant operated by EEW at Delfzijl. The CO_2 will be utilised to make e-methanol by OCI BioMCN in combination with the hydrogen from the electrolysers. The resultant e-methanol will be used as a bunker fuel for shipping.

SAF production requires hydrogen

Synthetic aviation fuel (SAF) is a broad term meaning the fuel has been derived from non-fossil origins. The largest source of SAF today is biofuel and the Finnish company Neste is a leading international producer. Plant oils are refined to yield aviation fuel that is suitable for high altitude operation on jet aircraft.

More than 300,000 commercial flights have used SAF in the past five years by more than 40 airlines. Thirteen major airports can refuel aircraft with SAF. Neste currently has a production capacity of 100,000 tonnes per year of SAF and by the end of 2023, Neste plans to produce around 1,500,000 tonnes each year. BP also has growth aspirations for SAF and already incorporates used frying oils into aviation fuel at their refinery in Lingen, Germany.

SAF is made from waste frying oils through a process called hydrodeoxygenation. Oxygen and sulfur are removed from the biologically derived feedstock using hydrogen. The resultant molecules are then isomerised to achieve the required property of the fuel. Distillation follows the isomerisation to ensure the SAF meets international standards, such as ASTM D756609 which specifies the requirements of aviation turbine fuel.

> "...methanol is around 20% more expensive to produce than ammonia for the equivalent energy value"

German legislation has been introduced that places a target of a minimum of 200,000 tonnes per year of SAF produced via the PtL pathway in 2030. This represents 2% of the aviation fuel that was consumed in Germany in 2019. The EU has proposed targets for both PtL fuels and other types of SAF.

Whilst biofuels dominate SAF production today, the next generation of SAF will be based on PtL. Hydrogen or syngas will be produced on electrolysers fed with renewable electrical power and combined with captured CO_2.

PtL relies on electrolysis and CCUS

Use of solid oxide electrolysis (SOE) can consume steam and CO_2 to yield syngas which can be converted to liquid hydrocarbons through established chemical pathways such as Fischer-Tropsch conversion. Sunfire GmbH, with its headquarters in Dresden, Germany has developed and commercialised its Sunfire-SynLink SOEC for this purpose. ▶

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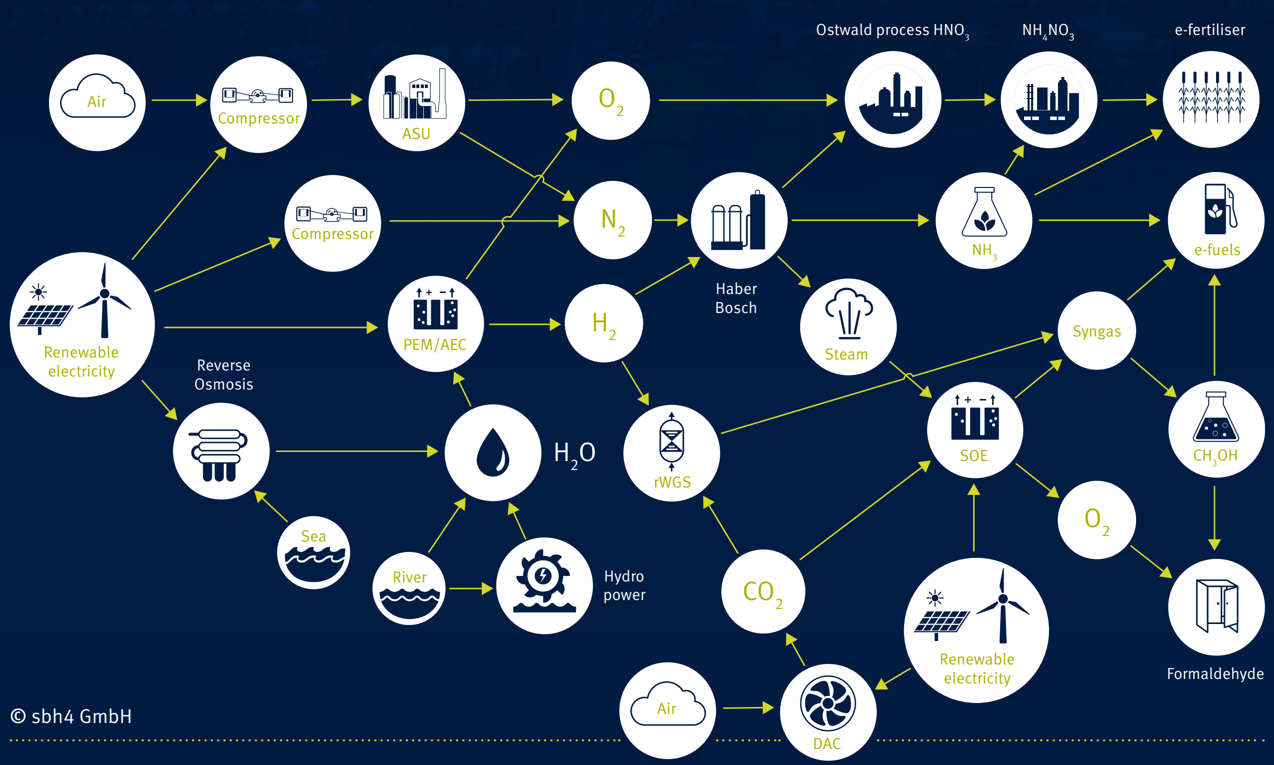

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Gerald Hammerschmid, Product Manager SOEC at Sunfire, says that the "introduction of steam to the SOE means that water molecules are delivered to the electrolyser in a highly energised state. Therefore, about 25% less electrical power is required to split them than when using low temperature electrolysis, such as a PEM or alkaline electrolyser."

In addition to the high efficiency, the Sunfire-SynLink SOEC is also very flexible, with a dynamic range of 5% to 100% and a hot-idle ramp time of less than 10 minutes. These parameters mean it can utilise steam from a wide range of processes.

On refineries, steel mills and thermal power plants, there is often waste heat or excess steam that can be fed to a solid oxide electrolyser to reduce the electrical power consumption. In PtL processes, downstream conversions such as Fischer-Tropsch or methanol synthesis are highly exothermic and can provide the heat requirement of the SOEC. This integrated pathway results in a high overall efficiency. "If no waste heat is available, it may be preferable to use an alkaline electrolyser to generate hydrogen," comments Hammerschmid. In addition to its SOEC range, Sunfire offers the Sunfire-HyLink Alkaline range for when low temperature electrolysis is required.

"The hydrogen from our alkaline electrolyser can also be reacted with captured CO_2 to yield syngas through the reverse water gas shift reaction, which can be converted to the required liquid hydrocarbons," Hammerschmid says, adding that "in both the SOE and low temperature electrolysis pathways, the required CO_2 can be captured from point source emissions or direct air capture facilities. The use of captured CO_2 reduces the overall CO_2 impact of SAF and introduces an element of circularity into the value chain."

Evidently, production of SAF via PtL is an emerging CO_2 utilisation application that could consume thousands of tonnes per year of captured CO_2. gw

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