

CEM FOR N₂O EMISSIONS CONTROL FROM AMMONIA-FIRED POWER GENERATION



Sustainable hydrogen and ammonia will be important power generation fuels in the future and are likely to progressively substitute natural gas. However, their emissions differ to natural gas and introduce continuous emissions monitoring (CEM) challenges that must be addressed to avoid greenhouse gas emissions.

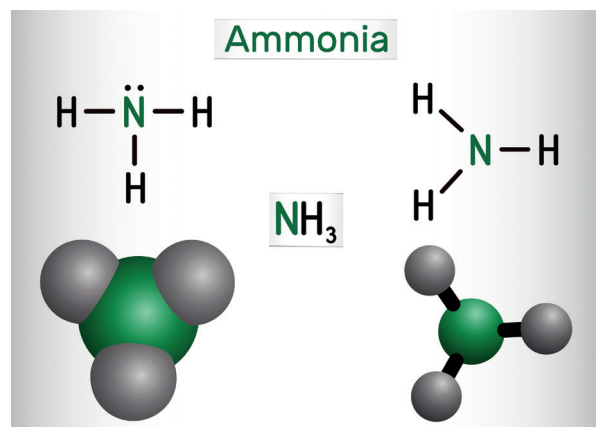
These new fuels and their emissions monitoring requirements will lead to equipment development challenges for solutions providers. They will also create opportunities to serve the market with new gas analysers and CEM systems.

The role of hydrogen in grid balancing

Hydro, wind, and solar power can decarbonise electricity production, but their temporal variability or intermittency results in a mismatch between power supply and demand. Batteries can support grid balancing over very short durations, but they are less cost-effective over the long term.

Converting excess power to a molecular energy store such as hydrogen or ammonia during peak renewable power generation periods and then using the hydrogen or ammonia to generate power on a turbine to meet peak power demand will be one way of balancing the grid over longer durations.

Hydrogen blending with natural gas and pure hydrogen fired gas turbines are being tested. Hanwha Energy tested 59.5% hydrogen blended with natural gas at their 80MWe gas turbine power plant in Daesan, South Korea. A 30% total NO_x reduction was reported



International shipping of hydrogen, hydrogen carriers and hydrogen derivatives

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	Compressed hydrogen gas	Liquid Hydrogen	Liquid Ammonia	Liquid Methanol	LOHC – Liquid Organic Hydrogen Carrier (MCH used as an example)	LNG, Liquefied Natural Gas
Temperature for transportation and storage	Ambient	-253 °C	-33.3 °C	Liquid at ambient temperature	Hydrogenation: 150-200 °C; Transported at ambient temperature; Dehydrogenation: 250-320 °C	-162 °C
Pressure for transportation and storage	250 bar	Close to atmospheric pressure	Close to atmospheric pressure	Close to atmospheric pressure	Hydrogenation: above 20 bar; Transported at atmospheric pressure; Dehydrogenation: below 5 bar	Close to atmospheric pressure
Density	0.017 kg/L	0.071 kg/L	0.68 kg/L	0.79 kg/L	0.77 kg/L	0.46 kg/L
Toxicity	non toxic	non toxic	TWA 25 ppm	TWA 200 ppm	TWA 400 ppm	TWA 1,000 ppm
Flammability (% in air)	4-74 %	4-74 %	14.8-33.5 %	6.0-36.5 %	1.2-6.7 %	4-15 %
Volumetric Lower Heating Value (LHV)(MJ/L)	2.43	8.52	12.7	15.7	5.76-8.5	22.2
Gravimetric LHV (MJ/kg)	120	120	18.6	19.9	7.48-11	48.6
Infrastructure readiness for large scale deployment in mid-term H/M/L	L	L	H	H	M	H
Commercialisation status and pilot projects	Global Energy Ventures, adapting CNG technology for compressed hydrogen shipping	HySTRA-Hydrogen Energy Supply-chain Technology Research Association – Australia to Japan LH2 shipping	Many commercial liquid ammonia production, distribution and storage assets worldwide with 120 ports locations able to handle ammonia	Methanol is a widely traded commodity with tankers up to 50,000 tonnes	The HySTOC (Hydrogen Supply and Transportation using Liquid Organic Hydrogen Carriers) project in Finland	Many commercial LNG production, distribution, storage and regasification assets worldwide

International shipping of hydrogen hydrogen derivatives and LNG frame

alongside a 22% reduction in CO₂ emissions.

Due to the relationship between H₂ blend composition and CO₂ emissions reduction, a high proportion of hydrogen is required to achieve significant CO₂ emissions reduction. Ultimately, pure hydrogen on the turbine would be the goal.

The hydrogen to Magnum project in the Netherlands proposes to burn pure hydrogen on three Mitsubishi Power M701F 440MW power blocks on the Eemshaven Magnum power plant, operated by RWE. The project will integrate underground hydrogen storage in multiple salt caverns to enable very long duration energy storage for long term grid balancing.

Ammonia as a transportable clean energy vector

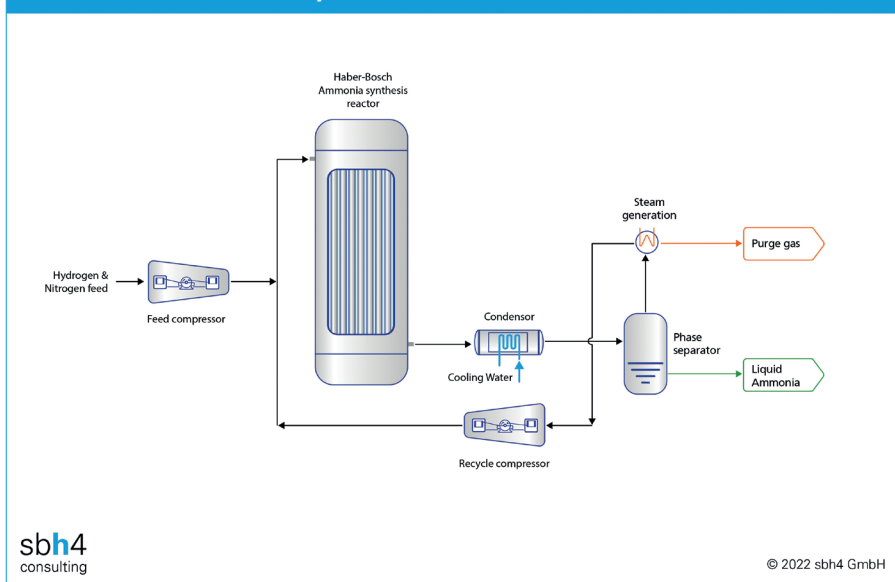
Hydrogen is very difficult to transport in large quantities over long distances. Linking energy importers with locations with abundant renewable power that can produce large quantities of low-cost

green hydrogen from electrolysis schemes or with CCS may require conversion of the hydrogen to ammonia, which is easier to transport by ship due to the high volumetric energy density of liquid ammonia.

Ammonia can be fired on gas turbines using various power generation cycles. The ammonia fuelled combined cycle can approach the natural gas fired IGCC efficiency. An alternative cycle known as CGHT can marginally improve on the ammonia combined cycle to come very close to the natural gas fired IGCC efficiency. In the CGHT, ammonia is decomposed to hydrogen and nitrogen using heat from the combustion process prior to the cracked ammonia being fed to the burner.

Ammonia-fired turbines are like those used with natural gas. The main changes are in the burner and the process control system, not the turbine itself. Control of NO_x emissions in general, and especially nitrous oxide (N₂O) which is a very potent greenhouse gas is a focus of development in this area.

Haber-Bosch Ammonia Synthesis Process



Haber-Bosch Ammonia Synthesis Process

Minimising and monitoring nitrous oxide emissions

Partial cracking of 20% to 30% of the ammonia is a solution that several turbine OEMs are testing. The blend of ammonia, hydrogen and nitrogen seems to burn very well.

When using 20 to 20% of cracked ammonia blended with ammonia on a gas turbine, optimisation of the air:fuel ratio is important to ensure efficient combustion with minimum emissions. Tests have shown that using a slightly oxygen rich flame, with an equivalence ratio of 0.8 to 0.9, can eliminate N_2O emissions. As the equivalence ratio falls to 0.6 N_2O emissions can rise to as much as 200 ppm by volume. At a ratio of 1.3, they would be around 50 ppm.

The National Institute of Advanced Industrial Science and Technology (AIST) is one of the largest public research organizations in Japan. They have conducted tests to validate the use of an ammonia natural gas blend for power generation on a small gas turbine. Co-firing ammonia with hydrocarbons changes the emissions footprint since CO and CO_2 may be formed.

In Japan, there is a large pilot project in planning which will co-fire ammonia onto unit 4 of the Hekinan coal fired power plant. The reduction in coal usage on this 1GWe unit will reduce CO_2 emissions since the ammonia will be sourced as green or blue ammonia. It will be important to avoid N_2O emissions since N_2O is an extremely potent greenhouse gas, about 250 times worse than carbon dioxide.

When co-firing ammonia with coal, or natural gas CO and CO_2 will be present in the flue gas. This adds to the complexity of the CEM system because CO and N_2O have overlapping peaks in the IR spectrum. The CO_2 IR absorption peak is also very close to N_2O .

The ISO 21258 (Stationary source emissions -Determination of the mass concentration of dinitrogen monoxide) has been developed to enable accurate measurement of N_2O in flue gas streams. It confirms NDIR as the reference method and draws attention to the need to convert CO to CO_2 and potentially to analyse the CO_2 on a separate instrument or channel and then compensate for CO_2 if required.

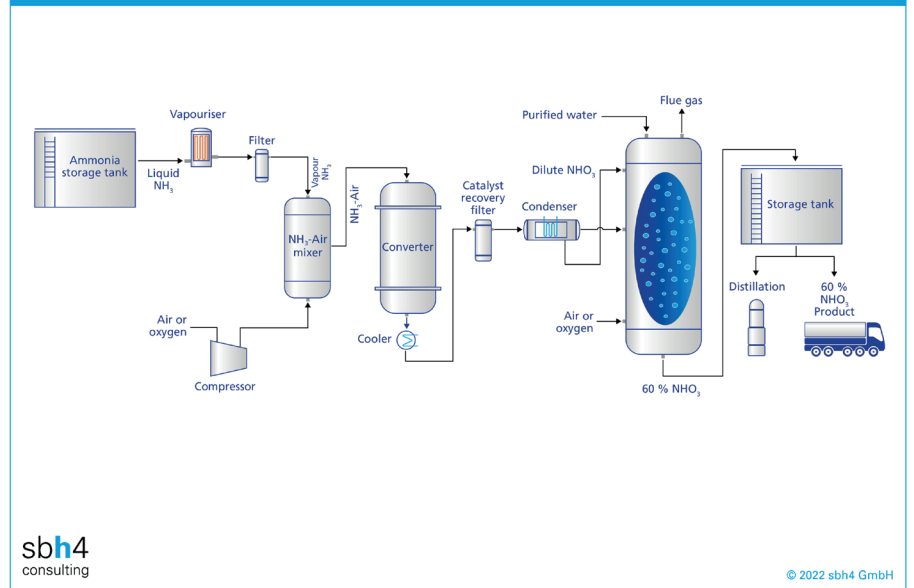
Commercial experience of CEM for nitrous oxide

Fortunately, there is relevant experience to draw on for N_2O flue gas analysis. N_2O is a regulated greenhouse gas in the European Emissions Trading Scheme (ETS) and is also regulated through US Greenhouse Gas (GHG) legislation. Nitric acid production has dealt with the challenge of CEM for N_2O for many years.

Commercial systems exist that can enable simultaneous N_2O and NOx analysis. As an example, the Fuji CEMS from Fuji Electric uses NDIR for the N_2O analysis. The SWG200 from MRU also uses NDIR as the method for N_2O analysis.

MKS offers their MultiGas FTIR with capability for N_2O analysis. The Rosemount CT5100 quantum cascade laser gas analyser

Ostwald Process for Nitric Acid Production



Ostwald Process for Nitric Acid Production



Hekinan power plant, Japan

has also been used for research into N_2O emissions from power generation turbines.

Ammonia may also be used as a fuel for aviation, maritime propulsion, and land-based mobility. In these cases, engine development and testing will require N_2O CEM systems and they may also be required to be installed on ships to monitor maritime emissions.

The growth of low-carbon fuels for power generation and propulsion will introduce new CEM challenges. It will simultaneously open new opportunities for innovative solutions providers to serve this emerging market.

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