Safe oxygen production for Giga-scale hydrogen generation

ASU design and operation relies on engineering expertise to ensure that the Giga-scale production of oxygen to make low carbon hydrogen is done safely

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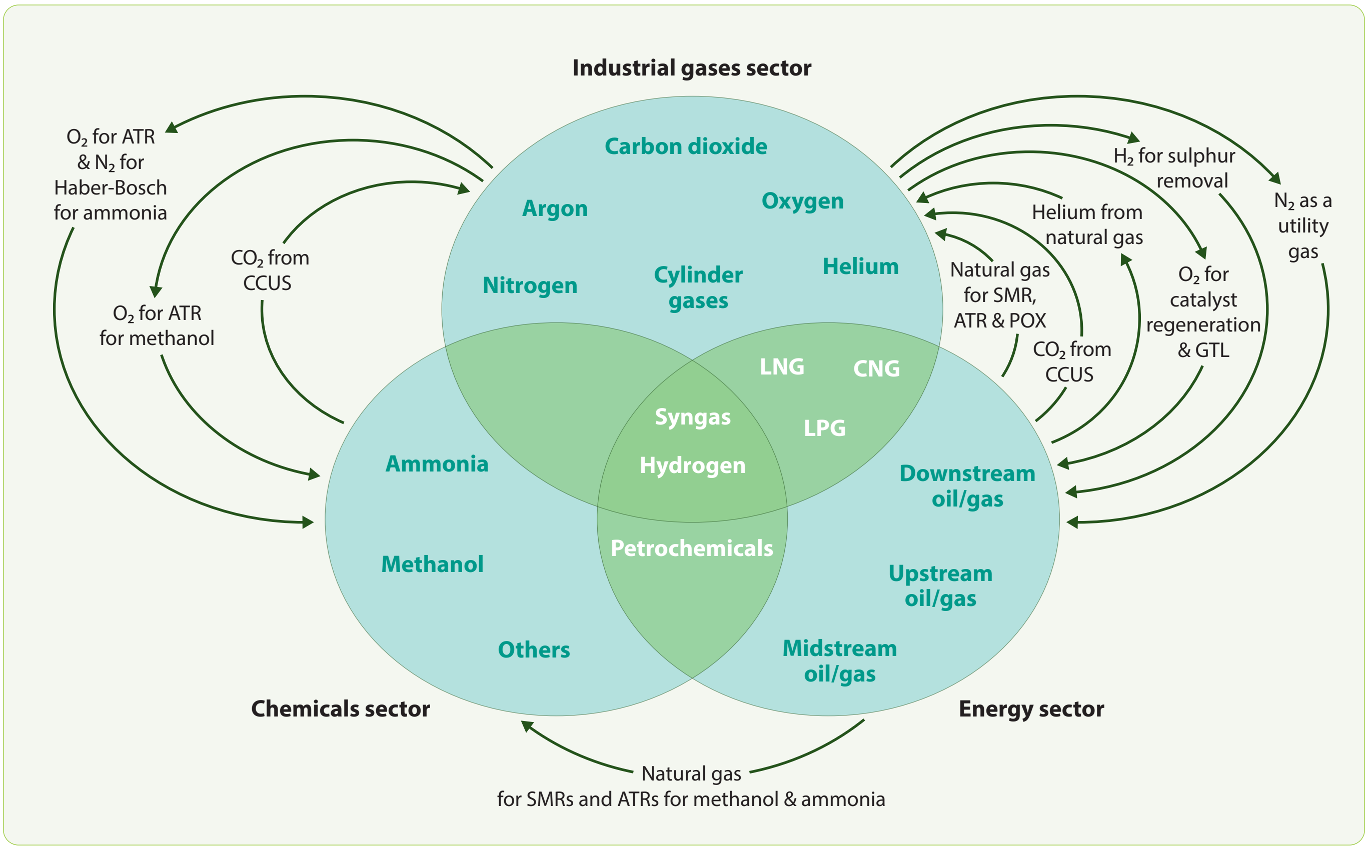
Oxygen is one of the main industrial gases and, at present, oil and gas processing and iron and steelmaking are the major consumers of oxygen worldwide. In the future, as there is a progressive decarbonisation of the energy sector, low carbon hydrogen production from natural gas and coal will be a major driver of growth in oxygen demand. Handling hydrogen comes with obvious hazards of flammability and explosion. The production of oxygen also requires the utmost respect for safety and best practices in operations and engineering.

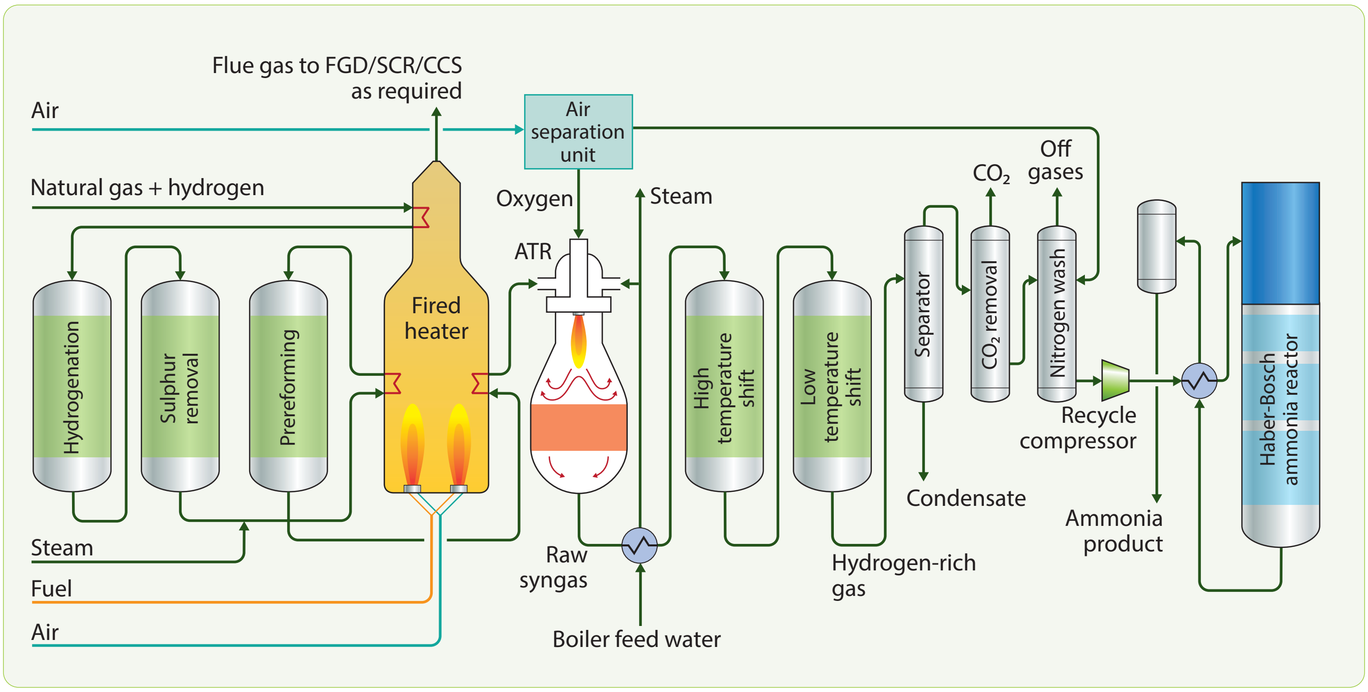
Oxygen is required to make low carbon blue hydrogen

As hydrogen production ramps up, we are leaping orders of magnitude from Mega-scale to Giga-scale projects. The largest hydrogen electrolysers operating today are in the 20 Mega Watt (MW) range. Plans already exist for Giga Watt (GW) systems. Scale-up is also the order of the day for hydrogen production from natural gas and coal.

As an example, the H2H Saltend project that is planned to support decarbonisation of the Humber industrial cluster in East Yorkshire, UK. It



The production of oxygen and other industrial gases is heavily integrated



Air separation units can provide oxygen to the ATR and nitrogen to the ammonia reactor in decarbonised 'blue-energy islands'

proposes a 600 MW autothermal reformer (ATR) to make hydrogen-rich syngas. Conventional steam methane reformers (SMRs) do not require pure oxygen. On the other hand, ATRs do. To enable 600 MW of hydrogen production, the air separation unit (ASU) would need to produce about 1200 tonnes of oxygen per day. That would make it one of the largest in the UK.

Producing hydrogen from natural gas using reformers means that carbon dioxide (CO_2) is generated from the process chemistry and the heat energy requirements. 'Blue hydrogen' is produced through the integration of carbon capture and storage (CCS) with the reformer. To qualify for the 'blue' hydrogen label, the captured CO_2 will be sent to a CCS scheme under the North Sea, where it will be stored underground permanently in natural geological formations.

CCS in the North Sea is a proven technology. Equinor commenced capture and sequestration of CO_2 on the Sleipner West field in the Norwegian sector more than 20 years ago. The components of a CCS scheme, from the absorption tower to the multi-stage CO_2 compressor with integrated drying system, are all highly developed.

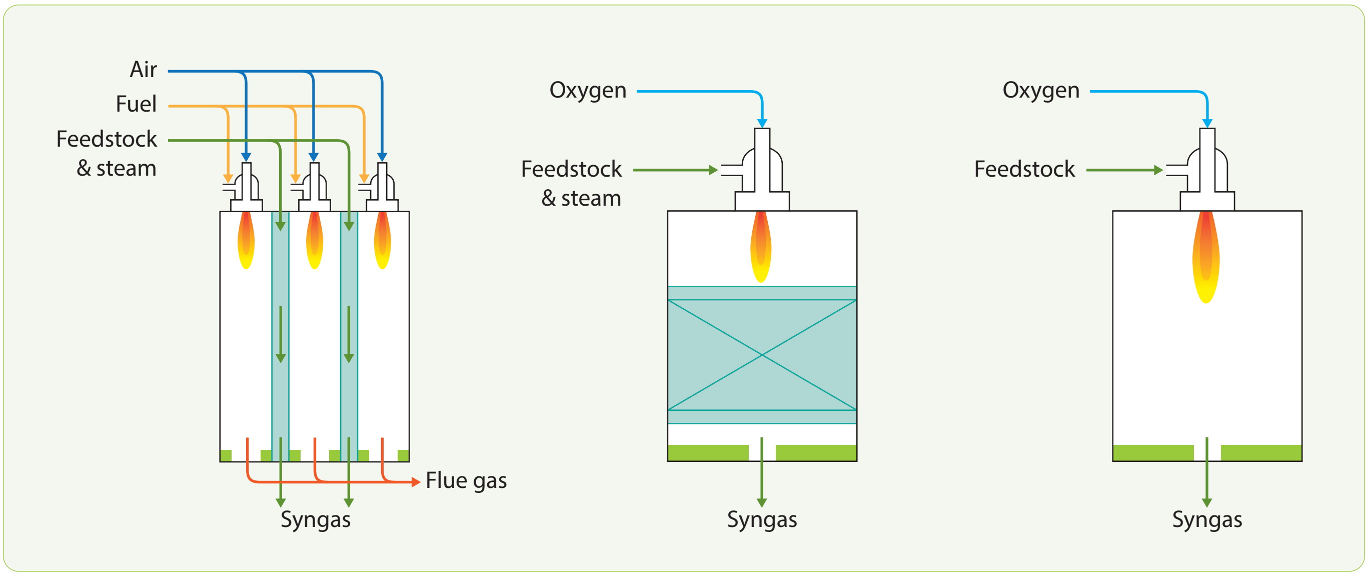
Beyond Norway, CCS, or carbon capture and usage (CCUS) combined with enhanced oil recovery (EOR), has also been used in Australia, Canada, and the United States for many years. Most major schemes have involved carbon capture retrofits onto existing carbon-intensive processes, such as decarbonisation of coal fired power plants and carbon capture from SMRs.

Since these have been retrofits projects, reforming technologies and CCS have been developed in parallel. They have never been optimised synergistically as an integrated process. Regarding blue hydrogen production, a paradigm shift is required: the system must be optimised in a holistic way.

Downstream of the reformer, some blue hydrogen schemes will also integrate a blue ammonia plant. Like hydrogen, ammonia is a carbon-free energy vector. Use of ammonia as a fuel will expand its range of applications and drive significant growth in ammonia demand. Ammonia production would require nitrogen as a feedstock to react with the hydrogen to make ammonia. The nitrogen could be produced on the ASU alongside the oxygen that feeds the ATR. The reforming, air separation and ammonia processes would be interdependent, and the integrated equipment can be viewed as a decarbonised 'blue-energy island'.

Giga-scale oxygen for gas-to-liquids

The use of natural gas and ASUs to make syngas for fuels goes beyond their proposed application to make hydrogen. In 2006, the Oryx gas-to-liquids (GTL) project in Qatar was built to add value to natural gas and produce liquid fuels as



SMR, ATR and POX technologies for hydrogen production from natural gas

energy-dense export products. Oryx has two large ATRs. Each is fed by a large ASU, rated at 3,500 tonnes per day of oxygen. The two ASU cold boxes for Oryx were built by Air Products at Acrefair in Wales. In a similar project, the Escravos GTL facility in Nigeria started up in 2014. It is of a similar configuration to Oryx, and it also uses two Air Products ASUs rated at 3,500 tonnes per day of oxygen.

Shell's Pearl GTL facility was constructed at Ras Laffan in Qatar, close to the Oryx plant, and started up in 2011. It is fed by eight Linde ASUs, each one rated at around 3,500 tonnes per day of oxygen to produce almost 30,000 tonnes per day. In contrast to Oryx, Pearl uses partial oxidation (POX) to convert natural gas to syngas. The use of POX natural gas gasification technology for GTL production was pioneered by Shell in 1993 at Bintulu on the island of Sarawak. At Bintulu, oxygen for the POX gasification reactor is supplied by a 3,200 tonne per day ASU supplied by Air Liquide.

Partial oxidation is like autothermal reforming because the reaction takes place in one unit, to which oxygen and natural gas are supplied. But it differs from both the SMR and ATR processes because neither catalyst nor steam are used. When wood, coal, or petcoke are used as feedstock, this process is called 'gasification'.

A subtle difference between the SMR, ATR, and POX processes is the pressure at which they operate. Whilst SMRs typically operate in the range of 15 to 40 bar, ATRs are more comfortable in the 30 to 50 bar range and POX reactors can operate up to 80 bar.

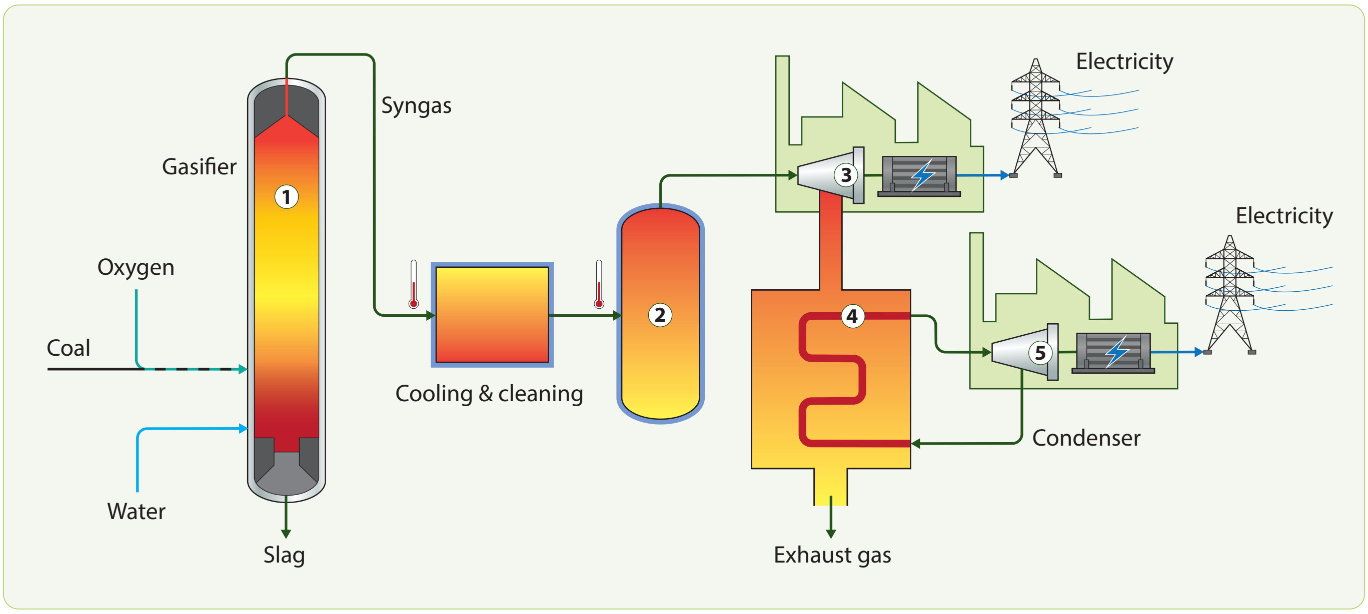
If hydrogen is intended for injection into gas transmission pipelines, producing it at high pressure is a tremendous benefit because a hydrogen compressor after the reformer can be avoided. This reduces both Capex and electrical power demand. This is one of the drivers for the selection of ATRs in proposed Giga-scale projects if an application of the hydrogen is to substitute natural gas to decarbonise domestic cooking and heating applications.

Hydrogen from coal gasification also pulls for Giga-scale oxygen supply

Beyond natural gas reforming and partial oxidation, coal and petcoke gasification is another Giga-scale pathway to make hydrogen-rich syngas. Gasification, like ATR and POX, requires oxygen. The use of pure oxygen, instead of air, is beneficial for precise control of the oxidation chemistry and avoids costly flue gas de-NOx systems. It also makes the integration of CCS more cost-effective because the system can be much smaller due to the avoidance of processing thousands of tonnes of nitrogen from the air.

One of the world's largest gasification projects will come into operation at Saudi Aramco's Jazan refinery where more than a dozen gasifiers built by Técnicas Reunidas will produce syngas from heavy refinery residues and petcoke. In total, the gasifiers at Jazan will be capable of producing 2 million normal cubic metres per hour of syngas.

At Jazan, the gasifiers will produce enough syngas to generate a total of 4 GW of power and steam. The syngas will be fired directly in gas



Pure oxygen from an air separation unit is required for coal, petcoke or heavy refinery residue gasification to produce hydrogen-rich syngas

turbines which produce 2.4 GW of electricity in an integrated gasification combined cycle, or IGCC power plant. The syngas-island will also export hydrogen and steam to the refinery. To feed the hungry gasifiers at Jazan, the process requires six Giga-scale ASUs supplied by Air Products, each one rated at 3,000 tonnes per day of oxygen.

Coal or petcoke gasification is a robust technology that can cope with oxygen at about 95% purity and the ASUs that feed gasification projects are generally optimised on this basis. The ASU can simultaneously produce nitrogen for refinery purging and inerting processes at a purity close to 99.999%.

Air Products has been instrumental in the Jazan refinery heavy residue gasification project and has secured their position in coal gasification through the acquisition of the GE Gasification business and Shell's coal gasification technology. The stated goal of these deals was not to become a technology licensor rather to enable the company to leverage gasification to win the associated ASU and syngas processing contracts as an integrated part of their industrial gases portfolio.

The Lu'an coal to chemicals project at Changzhi in China's Shanxi province, is one of the Giga-scale coal gasification investments that Air Products has made. Four gasification reactors have been constructed to supply syngas to the chemicals complex.

Purple hydrogen – coal gasification with CCS

The Hydrogen Energy Supply Chain (HESC) project in Australia will demonstrate the viability of ocean shipments of liquid hydrogen from Australia to Japan. It will open the door to full scale energy exports of low-carbon hydrogen. At this early stage of the project, hydrogen gas is produced from the gasification of brown-coal at a pilot plant in the Latrobe Valley in the Australian state of Victoria.

Gasification involves reacting coal with oxygen at a high temperature to produce syngas which contains CO_2, carbon monoxide, and hydrogen. This gas mixture is further purified to yield the desired hydrogen. The result is a high purity, low-cost hydrogen gas which can be cryogenically cooled to form liquid hydrogen for efficient long-distance transportation.

The 'brown' hydrogen produced in this gasification process is generated from coal and for every tonne of hydrogen produced on this pilot reactor 12 tonnes of CO_2 are generated. When the HESC pilot project is complete, a full-scale gasification plant incorporating CCS will be used to make the hydrogen production process more sustainable. Hydrogen produced from coal combined with CCS is sometimes referred to as 'purple' hydrogen.

Permanent underground CO_2 storage will be integrated with the CarbonNet CCS scheme. It aims to establish a commercial-scale CCS network in Victoria, Australia. The network will deliver CO_2 captured from a range of industries based in Victoria's Latrobe Valley, such as the HESC project and existing fertiliser plants. The main CO_2 transmission pipeline will be more than 100 km long with a 10 km offshore leg extending into the Bass Strait. CarbonNet has the potential to capture 5 million tonnes of CO_2 per year, giving it a similar scale to the existing Gorgon CCS project off the coast of Western Australia.

The CarbonNet CO_2 collection network is a complex 'hub and cluster' scheme where CO_2 will be captured from several plants and fed into a feeder network connected to a long-distance transmission pipeline. This concept mirrors existing natural gas pipeline grids. Similar CCS networks are proposed for the Zero Carbon Humber project in the UK and the PORTHOS scheme in Rotterdam, NL. The goal is to reduce the unit costs of CCS to enable affordable decarbonisation in support of the energy transition.

Hazards of oxygen production require careful mitigation

The hazards of hydrogen are well known. Furthermore, it is worth reflecting on the challenge of ensuring safe ASU operations to produce oxygen: there are inherent hazards, and the challenge is to minimise the risk. The devastated ASU site at the Henan Gas Group Yima coal gasification plant in Sanmenxia in China reminds us that ASU operations have the potential to lead to tragedy. Fifteen people lost their lives and 16 others were seriously injured in the explosion in July 2019.

The investigation at Yima concluded that "the direct cause of the accident was that the leakage into the cold box of the air separation device was not handled in time and 'sand explosion' occurred". The cold box then collapsed onto a 500 cubic metre liquid oxygen storage tank. Further explosions and fires followed.

The sequence of events after the cryogenic liquid leak into the cold box is understood but the events which caused that leakage are still not determined. However, the accident investigation report makes some pertinent recommendations such as controlling organic matter entering the main air compressor. It also recommends that the hydrocarbon content of the liquid oxygen system must be measured regularly. These points might cast some minds back to the horrific ASU explosion that took place at the GTL plant in Bintulu, Malaysia in 1997.

At that time, there were forest fires on the Island of Sarawak, where Bintulu is located. The smoke contained soot particles which accumulated in the cryogenic liquid oxygen reboiler on one of the ASUs. By coincidence, in the same year in China, an ASU at the Fushun ethylene complex, which produced oxygen to convert the ethylene to ethylene-oxide suffered a similar explosion. In this case, the root cause was abnormally high ethylene levels in the ambient air due to venting on the ethylene plant during a shutdown. In both Bintulu and Fushun, the combination of liquid oxygen, combustible hydrocarbon material, and aluminium, which is used to construct the reboiler, led to a massive explosion and fire. Process safety lessons have been captured in the EIGA doc 65/13: 'Safe operation of reboilers/condensers in air separation units'.

The principal precautions against hydrocarbon contaminant build-up in the cryogenic liquid in the ASU are well established and focus on CO_2 analysis at the warm end of the ASU and hydrocarbons analysis in the cryogenic liquid oxygen sump. Analysis of CO_2 break-through from the pre-purifier unit (PPU) is used to warn about the possibility that hydrocarbons such as methane or ethane are not being removed by the PPU and are also entering the ASU.

Analysis of hydrocarbons in the cryogenic liquid, generally by extraction of liquid oxygen from the main reboiler sump, is the second line of defence. This can be achieved using a total hydrocarbon analyser. Additionally, for ASUs that use reversing heat exchangers at their warm-end, routine analysis of acetylene in the liquid oxygen from the main reboiler sump is also required.

Reflecting on these issues is a stark reminder that ASU design and operation relies on engineering expertise to ensure that the Giga-scale production of oxygen to make low carbon hydrogen is done safely.

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