Ammonia absorption refrigeration for CO₂ liquefaction

Waste heat recovery for energy efficient CCS schemes

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here are many examples of how waste heat is recovered to ensure energy efficiency. For example, domestic condensing boilers recover low-grade heat from the combustion flue gases to pre-heat the returning central heating water optimise their energy efficiency for space heating applications.

Despite measures to recover as much usable energy from the process as possible, many industrial processes such as steel production, cement making, and power generation result in 'waste heat'. This is energy that is left over from the process which is available at lower temperature than can usefully be utilised in the main process. The waste heat is often released to the atmosphere via colling towers.

The concept of process integration means that waste from one process is used as a useful input to another. A fascinating example of waste heat utilisation is the use of high temperature heat pumps to elevate the temperature of waste heat to a useful level. For example, to generate steam at 120°C from waste heat at only 80°C. Another application of waste heat recovery is to drive a refrigeration cycle to create deep cold temperatures.

The ammonia/water absorption cycle is the technology that makes this possible. The operating principle relies on ammonia being highly soluble in cold water, but less soluble in hot water. A pump is used to recirculate an ammonia in water solution from a cold reservoir to another, where the mixture is heated – ideally using waste heat from another process.

As the mixture of ammonia in water is heated, ammonia is driven into the vapour phase at high pressure. The high-pressure ammonia can then be used in a classical condenser, expansion valve and vaporiser refrigeration cycle. Ammonia gas is then returned to the cold-water bath where it is re-absorbed into the water. The cold-water bath is chilled by heat exchange against cooling water to remove the heat energy from the refrigeration system.

Ammonia absorption chillers are being implemented for natural gas liquefaction by the Canadian startup Cool Science. Its founder, and inventor of their patented system, Colin Nikiforuk says that, "in contrast to classical vapour compression refrigeration cycles, the energy inputs are power for a pump and heat. The electricity demand, cost and maintenance requirements for the pump are less that those that are required for a gas compressor. The system can therefore offer cost savings and energy efficiency benefits."

Breathing new life into a centuryold technology

The basic technology related to ammonia/water absorption chillers has been known for 160 years. The earliest patent on the topic was prepared by the French inventor Ferdinand Caré in 1860. "Our innovations have made the process that Caré conceived more robust to operate and enable a lower temperature to be achieved, which means the technology can be applied to gas liquefaction and small-scale LNG," says Nikiforuk.

Cool Science has cemented its developments in a comprehensive patent, which has been granted in many jurisdictions. The system can cope with a broad range of ammonia purities and has minimal control points which makes is very easy to operate.

Nikiforuk adds, "We have turbocharged a technology that is more than a century old through implementation of modern engineering and process control fundamentals. Our modernised process, that we call MA3^{°°} refrigeration technology, builds on best practices that we have observed in similar processes in the refining sector."

Conventional CO₂ **liquefaction** For several decades, an established process of carbon dioxide (CO_2) capture, purification, and liquefaction has emerged. It is used extensively on biogas plants or breweries to yield CO_2 for industrial gases applications.

The first stage of the process involves the use of an amine solvent to absorb CO_2 from the biogas reactor or brewery fermenter. Then, the CO_2 is purified on an activated carbon adsorption bed to remove any traces of contaminants such as mercury or hydrogen sulfide.

Following the purifiers, the CO_2 is dried on a PSA (pressure swing adsorption) system loaded with a molecular sieve adsorbent material. This equipment is sometimes known as a regenerative dryer in this application and purified CO_2 from later in the process is used to purge the driers.

The last stage is liquefaction and purification. The dry CO_2 gas enters a condenser where it is liquefied to act as the reflux liquid in a distillation process. Operation of the condenser and distillation column at high pressure of around 20 bar means that the CO_2 can be liquefied using conventional mechanical refrigeration cycle chillers that operate at -30°C and can use ammonia as a refrigerant gas.

"As an alternative to the mechanical refrigeration cycle, which requires

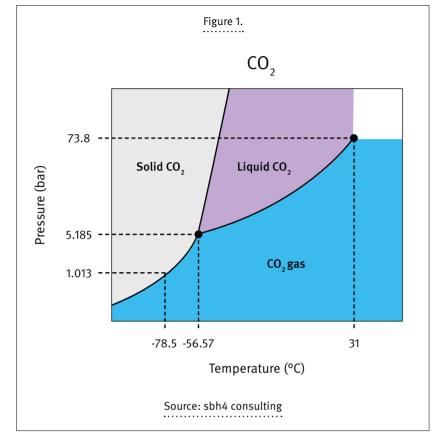
a large ammonia compressor, the ammonia absorption refrigeration cycle can be used to recover waste heat and reduce the power consumption of the process," adds Nikiforuk.

Integration of ammonia absorption technology into CCS schemes

At present, the majority of CO_2 liquefaction is conducted to create CO_2 as an industrial gas for commercial applications such as welding, food freezing or beverage carbonation.

In the future, it is possible that the requirement to liquefy CO_2 from carbon capture and storage (CCS) schemes for greenhouse gas emissions reduction will overtake commercial CO_2 capture as the main reason for CO_2 liquefaction. In some CCS schemes, the CO_2 can be compressed and transported to permanent underground storage location by pipeline. In many other





cases, this will not be an economically viable option due to the major capital investment required to develop the pipeline gas transmission infrastructure. In these cases, CO₂ will be liquefied and transported by road, rail, or ship from the emissions source to the storage location.

The dominant carbon capture technology at present is an amine based solvent process. CO_2 is absorbed into the solvent and then subsequently boiled out to regenerate the solvent in the reboiler of a stripping column. The reboiler requires abundant steam to drive the CO₂ out of solution.

One of the application ideas that Cool Science has for its ammonia absorption refrigeration cycle equipment is to use waste heat from the amine re-boiler steam to drive the CO_2 liquefaction process. "The challenge here, as with any process integration concept, is to match the temperatures and energy requirements of the two streams that are to be integrated," says Nikiforuk. He confirms that, "Our process modelling of several carbon capture process flow sheets indicates that significant power and energy savings can be achieved by using our technology in CO₂ liquefaction for amine-based CCS schemes."

Liquefaction of natural gas using ammonia absorption chillers

Classical refrigeration cycles that are used for LNG liquefaction rely on electrical power and mechanical compression energy as the inputs to the refrigeration cycle. The cold is achieved when hot compressed gases are cooled and then expanded. However, electricity is consumed, and power

is not always abundant in locations where natural gas or biomethane must be liquefied to LNG. This is especially true for small-scale LNG plants that may be in remote locations, away from the electricity transmission grid. The use of locally produced electricity from renewables to drive a mechanical refrigeration cycle may be possible but would require good sunlight or wind conditions. "In many places where methane liquefaction is required, such as Canada, we have neither the sunlight intensity nor the wind conditions that are required for renewable wind and solar power generation," says Nikiforuk.

"This is where the benefit of the ammonia absorption process comes to the fore – it can use waste heat from nearby processes, instead of electrical power, to drive the refrigeration cycle." Process integration allows energy efficiency, operating cost savings and contributes to sustainable LNG production.

LNG is used in a diverse range of applications. Beyond its primary roles as being a major traded international commodity for re-gasification and power generation, shipping is increasingly turning to LNG as a lowemissions bunker fuel to comply with maritime air quality requirements.

Liquefaction of excess natural gas to make LNG in upstream oil and gas operations is an alternative to flaring. Flaring methane avoids methane emissions, which is good because methane is a very potent greenhouse gas with a global warming potential 56 times worse than CO₂ on a 20year basis. However, flaring simply burns excess methane releasing CO₂ emissions to the atmosphere without recovering the energy value of the natural gas. So, liquefaction of excess methane to LNG is a win-win solution for avoiding methane and CO emissions at the well-head.

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