■ Technical Article

Small-Scale CO from CO_2 using Electrolysis

Reliable small and medium-scale CO production is costly and challenging, in contrast to the well-proven technologies available for large-scale applications. Haldor Topsoe has developed a stand-alone unit producing CO on-site and on-demand at competitive pricing. The unit is based on Haldor Topsoe's solid oxide electrolysis cell technology and uses feedstock carbon dioxide and electrical power to produce CO with high purity. The unit is cost competitive for most operations where the CO supply today relies on cylinders or tube trailers. Eventually, this technology opens up for a whole new segment of green and sustainable chemicals from renewable carbon sources.

Carbon Monoxide in Large-Scale Industrial Applications

Carbon monoxide is a highly toxic gas with a lot of industrial applications. It is one of the main gas constituents in syngas, used e.g. for methanol production. Many of the industrial applications require huge amounts of CO (>5000 Nm3/hr). Haldor Topsoe is well-known expert for large-scale CO production in reforming plants, as well as in designing processes where CO is used on a large scale (for example methanol synthesis). In these large-scale applications, CO is typically both produced and used locally within the plant. Previously, the hitherto smallest scale, about 1000 Nm3/hr, CO production used to be based on heat exchange reformers, with a membrane removing hydrogen. Thus, well-proven technologies are available for reliable CO production on large scale and Haldor Topsoe is a well-known licensor and catalyst supplier for these plants.

New Technology for Smaller Scale On-Demand CO Supply

For applications using CO on medium or smaller-scale (typically less than 1000 Nm3/hr), the supply options are more complicated and costly. Many companies having a need for CO on a regular basis have experienced the challenges involved in sourcing CO reliable and affordably. The number of merchant CO suppliers is limited, and ever-rising transportation costs and frequent production shortages only add to the headaches. For many smaller-scale users of CO gas (10-300 Nm3/hr), such as companies manufacturing polyurethane plastics, specialty chemicals, etc., there have been no alternatives to buying CO in large gas cylinders, typically in the form of tube-trailers, that are then parked next to the chemical plant until the cylinders are empty. Not only does this mean high costs for these customers, but also an increased safety risk from storing large amounts of hazardous CO on-site.

Industrial efficiency and safety continue to require innovations and changes to the way we perform all of our production, supply, transportation, and administration, and innovations to the CO supply can address the above customer pains and add significant value.

To address these customer pains, Haldor Topsoe has developed the electrolytic CO solution (eCOs) system, wherein CO is safely produced via the electrolysis of CO_2 at 700-85^{0}C using solid oxide electrolysis cell technology. On-site CO production is the answer for any distributor or end user needing a steady supply of affordable CO. Transportation of carbon monoxide may be reduced or completely eliminated with on-site CO production using eCOs.
On site CO generation is a significant development to the medical, pharmaceutical, metallurgy, electronics and specialty chemicals industries (which includes Carbonylation routes such as phosgene, polycarbonates, polyurethane, isocyanates etc.), which require carbon monoxide in their processes as well as to gas distributors. The eCOs technology ensures security of supply, eliminates the need to transport hazardous gas, and drastically reduces costs related to storage, rentals and connections.

The eCOs technology requires only a power source and CO_2 supply, which often already is established on-site, or is easily established as a commodity. With eCOs, CO can be produced effectively and efficiently. The specific benefits of eCOs are:

- On-site production on-demand
- Multiple sizes and purity options uto 99.999 per cent Grade 5.0 (main impurity CO_2)
- Fully replaces tube trailer or cylinder supply
- Cost savings compared to bottles and tube trailers
- Easy to operate for non-chemical operators

What is an eCOs plant

The name eCOs stands for "electrolytic CO solution", and the heart of an eCOs plant is a solid oxide electrolysis cell (SOEC). The eCOs plant flow diagram as shown in Figure 1 consists of two steps: 1) CO generation step (SOEC) and 2) gas purification step. In the CO generation step, the SOEC efficiently reduces CO_2 to CO through the electrochemical process of electrolysis. This results in a CO rich

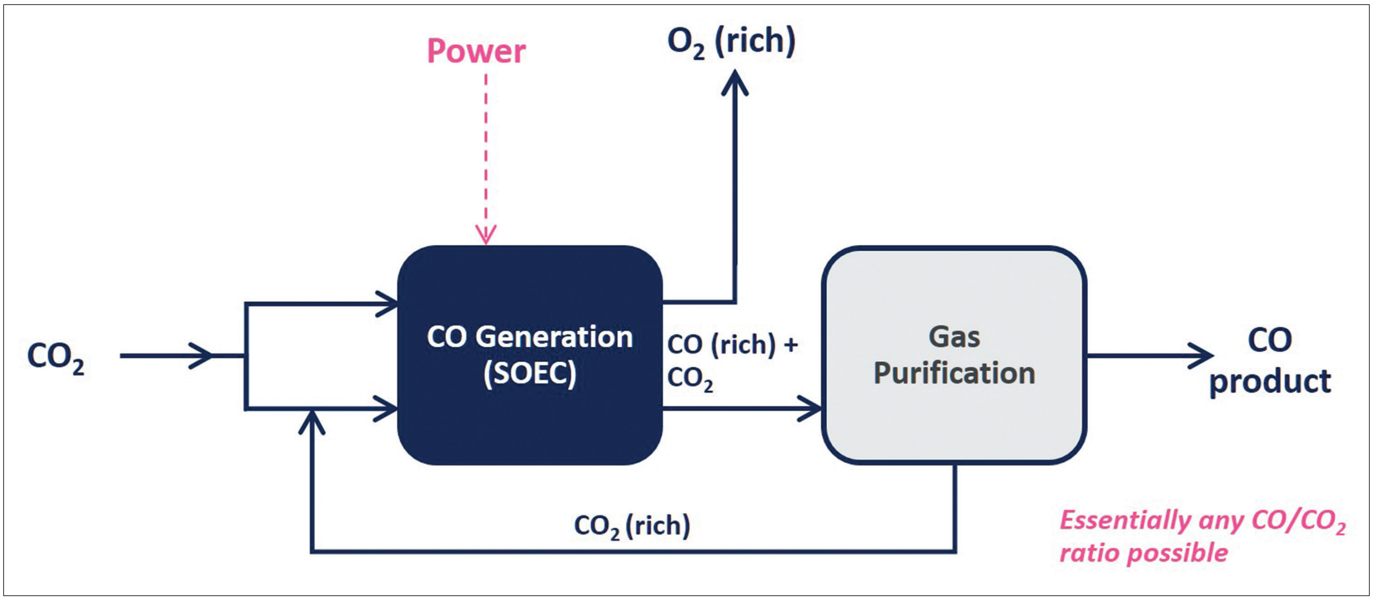

Figure 1: eCOs plant flow diagram

stream and an O2 rich stream. The O2 rich stream is vented to the atmosphere or can be exploited for other suitable applications. Any remaining unconverted CO_2 from the CO rich stream is removed from the CO product gas using a gas purification step. Removed CO_2 from the gas purification step, depleted in CO, is recycled back to the CO generation step.

Haldor Topsoe's experiences in fuel cells and separation technology have been the foundation of the development of the eCOs. That expertise has made the eCOs a safe, efficient, reliable, and cost effective system for the supply of CO, without personnel required by the users. The modular containerized design allows for plants as small as 6 Nm3/hr and as big as 200 Nm3/hr with turn down ratio down to 30 per cent. An eCOs plant is delivered as a stand-alone unit with power, CO_2 and product gas connections.

The eCOs technology ensures high levels of purity, producing CO ranging from 99.5 per cent to 99.999 per cent purity with minimal contaminants and CO_2 as the main contaminant. For some applications certain impurities normally occurring in merchant CO is virtually non-existing with CO produced with eCOs. For a 99.96 per cent purity grade CO produced with eCOs, most of the contaminants is CO_2 (330 ppm) and N2 (30 ppm). O2 and CH4 is typically <0.1 ppm, H2O <0.1 ppm and H2 <2 ppm. These contaminants are sometimes critical for certain processes where CO is used and would normally require 5N grade CO if produced with traditional technologies.

How SOEC Works

Solid oxide electrolytic cells (SOEC), is an energy conversion technology that can be operated to store or convert electricity and carbon dioxide as carbon monoxide and oxygen, with high efficiency and high reaction rates. The cells operate at relatively high temperatures (700-850 ^{o} C) to split carbon dioxide into carbon monoxide and oxygen using the heat and the SOEC cell, thereby self-cooling. The heat which is inevitably produced with electrical current is needed for the electrolysis process.

The SOEC consists of three parts: an electrolyte, an anode, and a cathode that are built up of various ceramic (or solid oxide) materials (Figure 2). A cathode of an electrochemical cell is the electrode where reduction reaction occurs, and an anode is where oxidation reaction occurs. Using external electricity, SOECs are able to electrochemically convert carbon dioxide to carbon monoxide at the fuel electrode (cathode). At the same time, pure oxygen can be obtained at the oxygen electrode (anode). The two electrolysis products, carbon monoxide and oxygen, are formed on each side of the cell.

At the cathode, CO_2 dissociates to form CO and O. The oxygen atom reacts with the incoming electrons from the external circuit to form an oxygen ion. The oxygen ion is conducted through the electrolyte to the anode. At the anode, the oxygen donates the electrons to the external circuit to form an oxygen atom. Two oxygen atoms finally combine to form an oxygen molecule at the anode side of the cell.

Industrial Experience

The first eCOs plant of capacity 12 Nm3/hr is currently in operation at Gas Innovations in La Porte, Texas (Figure 3). CO produced by the eCOs plant has surpassed the purity expectations of >99 per cent purity and demonstrated >99.9 per cent purity, with CO_2 being the main "contaminant".

"We have experienced a very stable daily production of CO on the eCOs unit, since we put it into operation in January 2016. The flexibility is outstanding and we can scale the production and choose the necessary

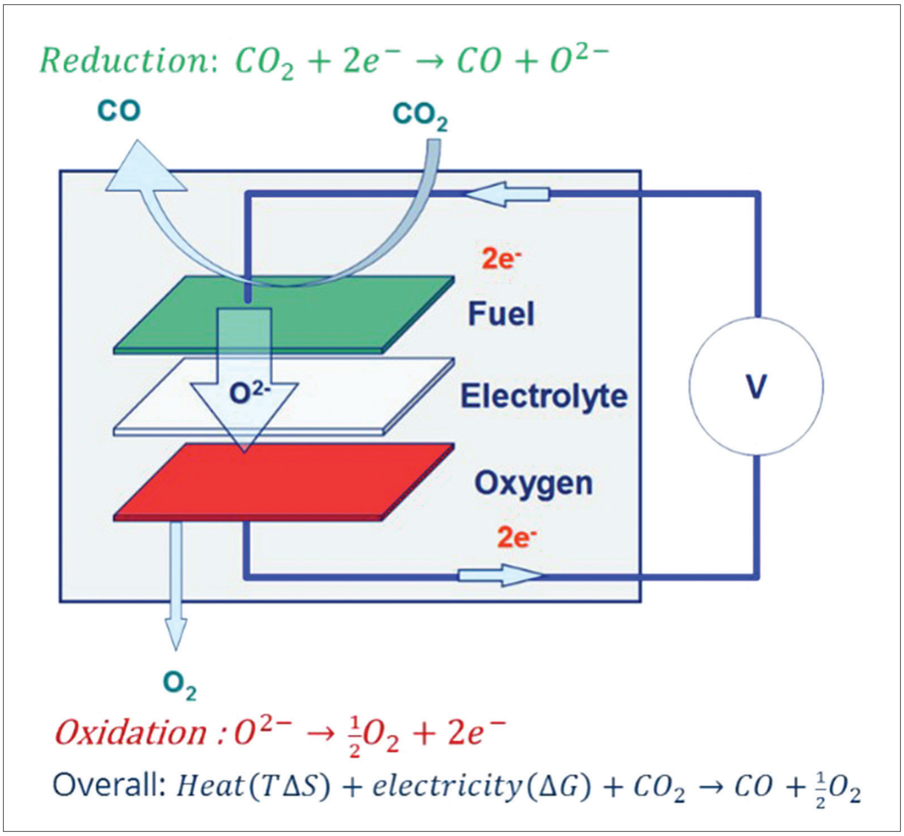

Figure 2: Basic operating principle of SOEC technology

purity for our needs at any given time. So we have chosen to sign a 15-year pay-per-use agreement with Haldor Topsoe for an additional eCOs unit with ten times larger capacity," says Ashley Madray, Executive Vice President, Gas Innovations. The new unit will be able to produce 96 Nm3/hr CO at up to 99.999 per cent purity and is expected to be online at the end of 2017.

Future Perspectives with SOEC

Besides CO_2 electrolysis, the SOEC technology has the future potential to be used in larger scale when the energy supply changes to more and more renewable resources. In order to achieve the climate goals of the Paris Agreement, global leaders at COP21 plan to rapidly increase the fraction of renewable energy supply towards 100 per cent over the coming decades. This will lead to significant changes in the electricity grid and a need for flexible large-scale energy storage due to the intermittent nature of wind and solar power.

Solid oxide electrolysis can be used to convert excess electricity to energy carriers such as hydrogen or syngas (H2 + CO), and Topsoe's SOEC technology can convert CO_2 and H2O to syngas by feeding steam (H2O) and CO_2 to the cells simultaneously. This is actually a specific feature of the SOEC technology and is not possible with conventional low-temperature electrolysis.

The syngas generated in this manner may be stored and later reconverted into electricity at peak demand. It could also be further processed to methane, which could be stored and distributed through the natural gas grid, or synthetic fuels used in the transportation sector. Another possibility is the production of green and sustainable chemicals from renewable carbon sources.

Figure 3: eCOs Plant at Gas Innovation Inc., La Porte, Texas, USA

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