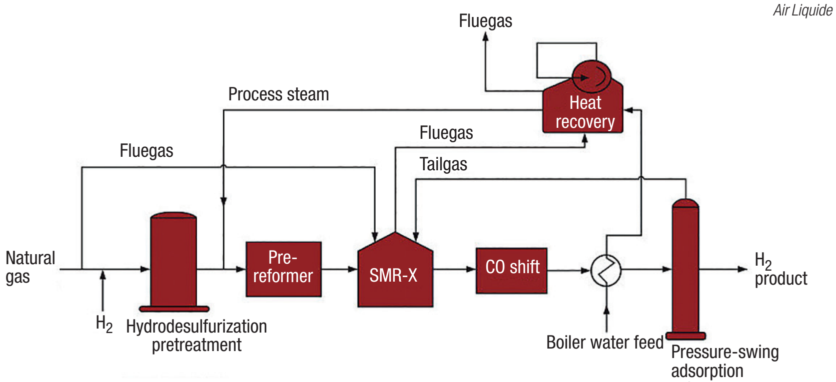
Making the Most of Methane Reforming

Despite valiant quests to find sustainable routes to syngas, methane reforming continues to play the lead — and 'greener' — role



Air Liquide

FIGURE 1. The SMR-X process produces H_2 without co-production of steam

For decades, the production of synthesis gas (syngas, H_2 + CO) from fossil-based feedstocks has been the key process for many sectors in the chemical process industries (CPI). Although energy efficiency has always been a driving force for making reforming technology more economical, the push today is toward reducing the carbon footprint of the plant. That means improvements in reformer design, heat integration and catalysts.

Also, "the shale gas boom in the United States was one of the biggest game changers in the past 10 years," says Christian Librera, head of Business Segment Syngas at Clariant Catalysts (Munich, Germany; www.clariant.com). Abundant and much cheaper resources have enabled the U.S. to significantly increase production of oil and natural gas. This has contributed to the fact that the U.S. will soon become a net exporter of methanol, and potentially ammonia, he says. "Further advantages to the U.S. are that methane-based syngas has a lower CO_2 footprint, and is more cost-competitive compared to China's coal-based syngas."

"In Europe, due to comparably high feedstock costs, the focus is on establishing more cost-efficient syngas production processes, and reducing related CO_2 emissions through different innovative technologies — energy efficiency is and will remain the prevailing theme," Librera continues. "In this context, renewables are also becoming more important, and are being explored to a larger extent than in other regions. Water electrolysis through renewable energy will play an increasingly important role in the future, as will syngas generated from biomass. All this will most likely happen gradually, rather than as a step change," says Librera.

In the meantime, traditional reforming will continue to play a leading role for the production of syngas. What follows is a small sample of some of the new process innovations for improving the efficiency of methane reforming, as well as some emerging technologies for the future.

Methane reforming

With the availability of abundant and inexpensive natural gas, the reforming of methane into syngas is of growing importance for the production ammonia, methanol, dimethyl ether (DME) and many other chemicals.

There are basically four main technologies used for reforming methane into syngas: steam-methane reforming (SMR), heat-exchange reforming (HExR), autothermal reforming (ATR) and partial oxidation (POX). Deciding which technology to use depends on a number of factors, including feedstock availability and desired product (For a good overview, see "A Guide to Methane Reforming," *Chem. Eng.* 2015, pp. 40–46). Today, SMR accounts for about 50% of the H_2 produced in the world. This highly endothermic reaction takes place in an array of catalyst-filled tubular reactors that are heated to high temperatures in a fuel-fired furnace.

Reducing steam export

One current trend in the industry is the requirement of minimum or zero co-produced steam from small to large steam-reforming units, says Alexander Rösch, director HYCO product line, Air Liquide Engineering & Construction (Frankfurt, Germany; www.engineering-airliquide.com). This results from efficiency programs in petroleum refineries and improvements of technologies, and is addressed by several technology bricks, like pre-reforming (single or multi-stage), heat integration, or new technologies. "As part of our portfolio of hydrogen technologies, we have recently developed SMR-X, a next-generation technology that produces H_2 without co-producing excess steam," says Rösch. Compared with conventional SMR, SMR-X features higher thermal efficiency at low steam co-production ratios and emits lower levels of CO_2, he says.

With SMR-X (Figure 1), the feed

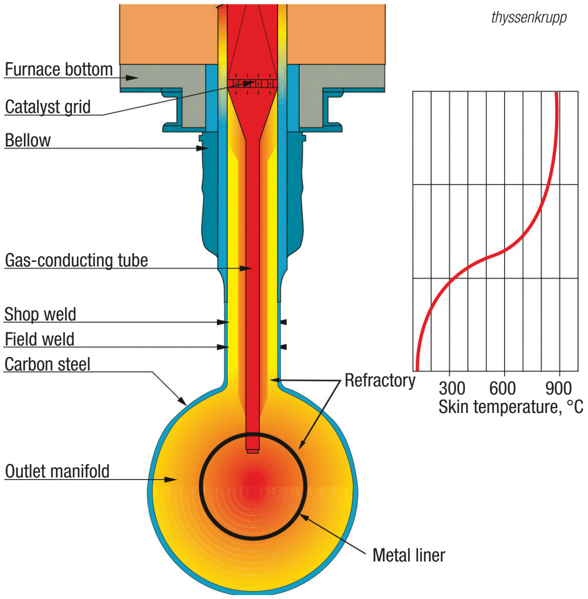


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FIGURE 2. The proprietary Uhde cold-outlet manifold system uses standard carbon steel instead of expensive heat-resistant austenitic steels

gas is transformed into H_2 through a reforming process driven by heat (700–900°C). Instead of generating steam from excess heat, the reformer tubes have been optimized to re-use the energy in the reforming process, Rösch explains.

"SMR-X technology provides lower production cost through internal process-heat recovery. While the bulk of heat to SMR-X is provided via radiative heat transfer, around 20% of the process heat is supplied by internal heat exchange. This results in reduced furnace size and fewer reformer tubes compared to traditional steam reformers. Additionally, the internal steam system design is simplified, since no steam is exported," Rösch says.

With SMR-X, Rösch continues, the desulfurized feed gas is mixed with process steam, and passes through catalyst-filled reformer tubes and is then cooled by heat exchange with process gas inside the tubes. Overall feed and fuel consumption, as well as CO_2 emissions are reduced by 5% compared with a conventional SMR, he says.

Last year, Air Liquide and Covestro AG (Leverkusen, Germany; www.covestro.com) signed a long-term contract for the supply of hydrogen at Covestro's production site in the port area of Antwerp, Belgium. Air Liquide will invest €80 million in the construction of a "new generation" H_2-production unit. The plant will be fitted with SMR-X technology. The H_2 produced will also enable Air Liquide to supply customers in this industrial basin in Europe. In connection with this new long-term contract, the H_2 will be used in the production of aniline, which is one of the base chemicals for polyurethanes. This new SMR-X unit is expected to start operation in 2020.

Marco Scholz, head of Process Group Hydrogen and Syngas OU Refining & Petrochemicals, thyssenkrupp Industrial Solutions AG, Business Unit Chemical & Process Technologies, (Dortmund, Germany; www.

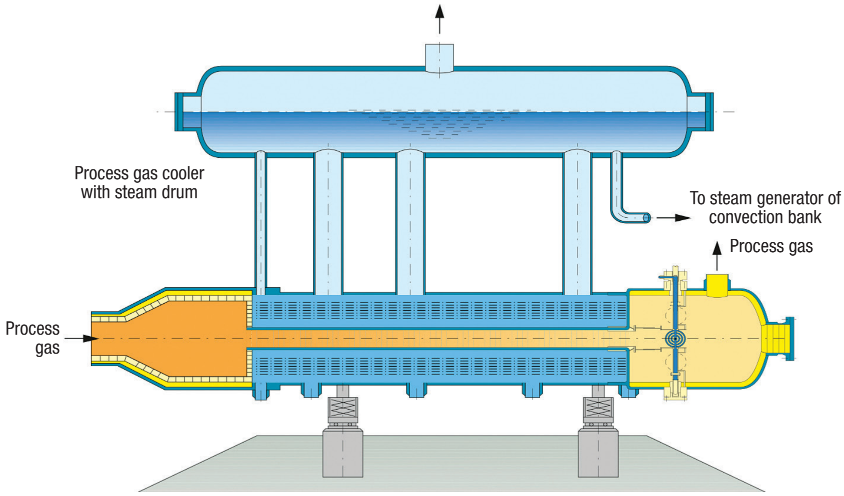

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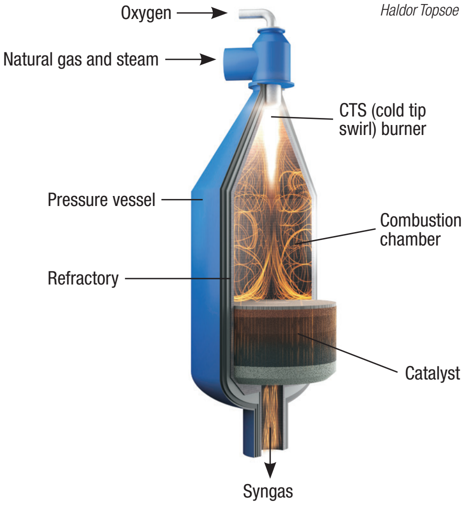
FIGURE 3. The heart of heat integration is the process gas cooler/HP steam generator, in which clean, high-pressure (HP) steam is produced by cooling process gas from the reformer



Haldor Topsoe

FIGURE 4. The heart of the SynCOR process is the autothermal reformer, which uses pure oxygen to convert CH_4 into syngas operating at a low carbon-to-steam ratio of 0.6

thyssenkrupp-industrial-solutions.com) agrees that a current trend in H_2 production by SMR is the design and building of low steam exporting plants with minimized feed and fuel consumption. "High-pressure (HP) steam is normally always produced as a byproduct in steam reformer plants. Reducing the feed and fuel consumption decreases the annual opex (operating expenditures) of the SMR plant. The overall efficiency of the plant is even higher when a certain amount of HP steam is exported. It can be used for driving large rotating equipment, as well as for heating or reaction purposes," says Scholz.

SMR plants from thyssenkrupp feature a dual steam system that allows steam production with guaranteed higher quality of export steam. Steam generated from process condensate is exclusively used within the steam-reforming process. This totally eliminates the need to return process condensate to a boiler feed-water-treatment unit (for example, a stripper) and reduces the amount of volatile organic components, explains Denis Krotov, senior process engineer and product manager at thyssenkrupp.

Thyssenkrupp Industrial Solutions invented the cold outlet manifold (Figure 2), which is applied in numerous NH_3, H_2 and methanol plants built by the company, says Krotov. To further improve the heat distribution within the concrete of the outlet manifold, thyssenkrupp currently applies an eccentric outlet manifold and a special design of transition piece from reacting tube to outlet manifold ("gas conducting tube"). Consequently, the surface temperature of the pressure shell is well balanced and thermal expansion is very even so that resulting thermal tensions are minimized and unwanted hot spots are excluded, explains Krotov.

The heart of the heat integration is the process gas cooler/HP steam generator (Figure 3). In this apparatus, clean HP steam is produced by cooling process gas from the reformer and functioning as a natural circulation boiler. The process gas cooler has an integrated bypass system and is maintenance-free. Its functionality has been proved in numerous projects, says Scholz. "Depending on the customer's request, the steam pressure and the degree of superheating can be selected as desired."

Autothermal reforming

"To meet the growing demand, future methanol plants will incorporate large capacities coupled with low production costs, high energy efficiency and the lowest possible environmental pollution," says Scholz. "Autothermal methane reforming (ATR) combined with energy-efficient methanol synthesis and distillation processes is the answer to these requirements," he says.

ATR uses pure O_2 to partially oxidize methane into syngas. This reaction is very exothermic, and takes place at very high temperatures (950–1,050°C, compared to 750–959°C for SMR), which requires robust catalysts. Haldor Topsoe A/S (Lyngby, Denmark; www.topsoe.com) pioneered advanced ATR in the 1990s, and commercialized its low steam-to-carbon (S/C) ATR for smaller-sized units in 2002. Recently, the company introduced its SynCOR technology. The core of the SynCOR process is the ATR (Figure 4) that reforms methane into a syngas with S/C ratio of only 0.6, which means the steam throughput is reduced by 80% compared to conventional SMR plants, says Svend-Erik Nielsen, a fellow at Topsoe. The SynCOR process is applicable for a number of downstream products, such as NH_3, methanol, H_2, gas-to-liquids (GTL), CO, formaldehyde, DME and other chemicals.

With the trend for building large, single-train plants, economy of scale is very important, and ATR offers unique scaleup advantages over SMR. Unlike SMR, which requires increasing the number of reformer tubes for scaleup, an ATR scales up on the diameter of the reactor, explains Nielsen. "This means the capital expenditures (capex) for a ATR plant are significantly lower than that of a SMR for large plants," he says.

The most recent addition to the SynCOR family is SynCOR Ammonia, which makes it possible to use ATR for single-train ammonia plants with a capacity of 6,000 metric tons per day (m.t./d). This has been made possible with the commercialization of Topsoe's latest high-temperature shift catalyst, SK-501 Flex, which uses a promoted zinc/aluminum spinel structure instead of the traditional iron/chromium structure. It removes the risk of forming Fischer-Tropsch byproducts at low steam-to-carbon ratio, which is a limitation of the traditional high-temperature shift catalyst, and thereby enables NH_3 producers to save on feedstock and energy, or boost production by up to 5% in their existing set-up in a revamp situation. The new catalyst also eliminates the risks related to handling of Cr^{6+}, both to the environment and plant personnel, says Nielsen.

New catalysts

"Our latest innovations, the steam methane reforming catalysts, ReforMax 330 LDP Plus (standard) and ReforMax 210 LDP Plus (lightly alkalized), were developed to solve our customers' challenges of increasing feedstock prices and energy costs by enhancing the efficiency of plant operations," says Clariant's Librera.

Chemically based on the industry-proven ReforMax LDP series, the catalysts' new and unique eight-hole flower-like shape (Figure 5) is designed to optimize catalyst geometry and mechanical strength. This results in a drastically reduced pressure drop (of up to 20%) across the reactor tubes compared to the previous catalyst generation, without compromising activity or stability, explains Librera. The design allows increases in gas throughput (by up to 11%), lowers greenhouse-gas emissions and leads to significant energy savings, he says.

The new ReforMax LDP Plus catalyst series has already demonstrated its performance advantages in several commercial facilities, including H_2 units in the U.S. and two major NH_3 plants in Europe. The facilities are benefitting from the expected pressure drop reduction across the catalyst bed, leading to a significant increase in energy efficiency — contributing to minimizing CO_2 footprint while also improving the cost competiveness of the plant, says Librera.

Another way to reduce pressure drop in steam reformers is the Catacel SSR catalyst from Johnson Matthey plc (JM; London, U.K.; www.matthey.com). In the Catacel SSR system (*Chem. Eng.*, March 2010. p. 11), which JM acquired in 2014, alloy strip is formed into engineered supports called fans, which are coated with a nickel-based steam-reforming catalyst. The fans are stacked inside of the reformer tubes. This design offers many advantages over traditional ceramic pellets, and provides lower pressure drop, high heat transfer and high activity, says the company. Catacel SSR is said to represent the single biggest step forward when it comes to the development of catalyst shape. Compared to standard pellets, Catacel SSR leads to a 20% decrease in pressure drop. "The value of increased throughput when exchanging an old catalyst with a new optimized one can in some instances pay for the optimized catalyst charge in less than one year, says the company.

The last two years have seen a commercial breakthrough for the technology from the initial adopters in 2008, with smaller reformers (containing up to ten tubes), to conventional reformers, a market where

Clariant Catalysts

FIGURE 5. The eight-hole flower-like shape of the ReforMax LDP series catalyst is designed to optimize catalyst geometry and mechanical strength, and results in a reduced pressure drop across the reactor tubes

there are up to a thousand tubes in a single reformer, says Michael Hepworth, engineering technology manager at JM's Catacel Technology Center in Ravenna, Ohio. As of late 2018, Catacel SSR is operating in eight reformers globally, including an over 50-tube and an over 90-tube conventional, top-fired reformer. Product is being manufactured for two more conventional reformers with over 100 tubes, establishing SSR in the wider reforming market, says Hepworth. "This has resulted in continuous, two-shift operation at JM's Ravenna manufacturing facility," he says. (This technology is one of the six finalists vying for the 2019 Kirkpatrick Chemical Engineering Achievement Award.)

Dry reforming

Methane conversion with CO_2 instead of steam (dry reforming) is an alternative route from methane to syngas. With this technology, CO-rich syngas can be generated as an important feed to form many products or intermediates, such as organic acids, phosgene, polycarbonates and agricultural chemicals. On-site production of CO via CO_2-reforming of methane can be favorable due to economic and (transport) safety aspects, says Clariant's Librera. "Furthermore, the CO_2 footprint of the production site can be significantly reduced. Clariant provides a set of highly efficient catalysts for this application, and works in close cooperation with a reputable engineering partner for more than 20 years," he says.

Next year, BASF AG (Ludwigshafen, Germany; www.basf.com) and technology partner Linde AG (Munich, Germany; www.linde.com) plan to launch a new dry-methane-reforming catalyst (*Chem. Eng.*, February 2019, p. 9). To perform dry reforming, BASF developed two spinel-type catalysts based on nickel and cobalt. In addition to reducing the steam demand by up to 60%, dry reforming produces a CO-rich syngas ($CO:H_2 = 1:1$), which is optimal for directly making DME. A new catalyst system — a combination of two catalysts that perform bifunctional catalysis — is also being developed for the direct conversion of syngas to DME. The zeolite-based catalyst system also has a "self-cleaning" feature that prevents deactivation, says BASF. Commercial launch of the syngas-to-DME catalyst is planned for 2022.

Meanwhile, Japanese researchers are also working on new catalysts for performing dry methane reforming at low temperatures (*Chem. Eng.*, May 2019, p. 11). Although dry reforming has the potential to reduce CO_2 emissions, it is also prone to carbon deposition, especially at lower temperatures. The catalyst — a metal/oxide nanocomposite with tailored 3-D topology — is being developed at the National Institute for Materials Science (NIMS, Tsukuba City, www.nims.go.jp), in collaboration with scientists from the Kochi University of Technology and Tokyo Institute of Technology. In laboratory studies, the catalyst was shown to activate CO_2 and CH_4 at 623K, and promote low-temperature dry reforming at 723K for over 1,000 h — ten times longer than traditional supported catalysts.

Electrical heating

Another way to reduce CO_2 emissions from SMR is to use electrical heating instead of conventional fossil-fuel-fired furnaces. This is becoming more feasible as the cost and reliability of renewable electricity (wind or solar power) becomes available.

Last month, researchers from the Technical University of Denmark (Lyngby; www.dtu.dk) the Danish Technological Institute (Tåstrup; www.dti.dk) and Haldor Topsoe reported their studies on a compact, electrically heated reformer in the journal *Science*.

The laboratory reactor consists of a FeCrAl-alloy tube, which is coated on the inside by a 130-µm nickel-impregnated catalytic washcoat. The catalyst is directly heated by passing an alternating current across the two ends of the tube (resistive or Ohmic heating). Feed gas — a mixture of CH_4, H_2O and H_2 — passes through the reactor and is reformed into syngas at a temperature of up to 800°C. The electrical heating is reported to supply a nearly constant heat flux, which keeps the gas mixture near equilibrium and results in a better utilization of the reactor volume compared to conventional reformers. It also limits carbon formation.

The technology has the potential to reduce the size of SMRs by a factor of 100.

BASF, together with Linde and academic partners, is also developing an electrically heated furnace ("E-Furnace") for high-temperature catalytic reactions. Although the main target for this low-voltage, high-current furnace is for reducing the CO_2 footprint of catalytic crackers, the technology is also suitable for SMR. When combining the E-Furnace with dry methane reforming, syngas production could actually become a net CO_2 *consumer* of up to 490 kg CO_2/TNm^3 of syngas, compared to 350 kg CO_2/TNm^3 *emitted* by conventional reforming, says the company.

In another long-term research project, BASF, together with Linde, thyssenkrupp and academic partners, is developing furnace technology for pyrolyzing methane into H_2 and carbon. The process is said to require significantly less energy than the water electrolysis, and the solid carbon product can be used in the aluminum, steel and other industries. Laboratory studies have already been conducted using a moving-bed reactor that is heated by electrical induction. The second three-year phase of this project is now underway to further develop the proof-of concept for the reactor design and the carbon outlet. ■

Gerald Ondrey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