Options for economical supply of hydrogen

Peter Neumann
Florian von Linde

The use of hydrogen, especially for annealing applications, is steadily increasing. Hydrogen supply can be provided by trailers or by on-site generation. For hydrogen demands up to 300 m^3/h conventional generation processes and supplies are being increasingly substitued by advanced steam reforming. The on-site hydrogen generation using the HCE Ultra process provides advanced and fully automatic H_2 supply. This process requires only a minimum of investment costs, and is therefore an economically attractive solution.

Dr.-Ing. Peter Neumann, Manager Product Development; *Dr. Florian von Linde*, Managing Director; **Caloric Anlagenbau GmbH,** Munich, Germany.

The use of hydrogen, especially in connection with annealing applications, is steadily increasing. Raising the hydrogen concentration in a mixture with nitrogen results in a higher product quality. As a side effect, the annealing time of coils in bell-type furnaces can be shortened, since a low density of hydrogen improves the heat transfer inside the coil.

The hydrogen requirement for a bell-type furnace is mainly influenced by three factors. Depending on the surface contamination of the coil 1.5 up to 3.0 m^3 H_2 per t charge is required. (Unless otherwise stated in this article the gas volume is given in m^3 (s.t.p.)) Typically, the coil inventory of the furnace is about 50 to 200 t and the annealing process will take about 25 to 35 h. Considering the average figures for each factor, the hydrogen requirement for one bell-type furnace is approximately 10 m^3/h. With an increasing number of furnaces, the H_2 requirement generally rises. Depending on the specific conditions, any of the below supply options migth be the most economical solution in a particular case. The options are supply by trailers, by on-site generation using electrolysis, methanol reforming or steam reforming.

Conventional hydrogen supply

Hydrogen supply from outside by trailer. The economy of compressed or liqufied H_2 depends on the cost of transportation and on the distance between the source of H_2 and the end user.

Electrolysis. In the electrolysis process, water is split into hydrogen and oxygen by electric energy:

$$H_2O + \text{electric energy} \rightarrow H_2 + {}^1/_2\, O_2$$

Hydrogen is obtained with a purity of approximately 99.9 vol. %. The oxygen content and the moisture of the hydrogen generated requires a DeOxo step and a dryer in order to make the H_2 applicable as a protective atmosphere.

Electrolyzers are simple in operation and moderate in investment costs. However, with a consumption of typically 4.1 to 5.0 kWh per m^3 H_2 generated, they are expensive in operation. Except for locations with extremely low-cost electricity, electrolyzers are only viable ***for small H_2 requirements*** (typically up to 50 m^3/h).

Methanol reforming. Methanol reforming splits methanol and steam into a synthesis gas in the presence of a copper-zinc catalyst.

$$CH_3OH + H_2O \rightarrow 3\, H_2 + CO_2$$

The process typically takes place at high pressures of up to 25 bar and temperatures between 250 and 300 °C. High-purity hydrogen, typically 99.999 vol.%, is achieved by using a pressure swing adsorption (PSA) unit (**figure 1)**. The main utilities for the process are methanol and demineralized water. For the production of 1 m^3 H_2, approximately 0.65 kg methanol is required.

Methanol reformers (**figure 2)**, are moderate in investment costs, complexity and utility costs. They are preferably applied at locations without access to natural gas and for typical capacity ***ranges from 50 to 3000 m^3/h***.

High-temperature steam reforming. With the steam reforming process **(figure 3)**, hydrocarbons such as natural gas, LPG or naphtha are mixed with steam and converted to a ***synthesis gas*** in the presence of a nickel catalyst. This conversion is an endothermic process.

$$C_nH_m + n\,H_2O \rightarrow n\,CO + (m/2 + n)\,H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Depending on the feed used, this reaction typically takes place at temperatures between 800 and 900 °C and pressures of up to 30 bar.

In an additional catalytic process step, the hydrogen yield in the synthesis gas is increased. This is achieved by shifting the water-gas equilibrium to lower temperatures of about 400 °C, using the surplus of water vapour remaining in the synthesis gas. This CO shift reaction is exothermic.

$$CO + H_2O \rightarrow CO_2 + H_2$$

The synthesis gas generated in this reaction consists of the main components H_2 and CO_2 and smaller amounts of CO, CH_4 and remaining water vapour.

Upstream of the reforming step, a feed treatment unit is installed to remove sulphur components from the natural gas feed, which would otherwise poison the reforming catalyst.

The steam required for the reforming process is generated by a waste-heat boiler integrated into the process. Depending on the design, it is possible to export the surplus steam. After the CO shift reactor, the synthesis gas is cooled down to ambient temperatures and is sent to the hydrogen purification unit. The purification step uses a pressure-swing adsorption unit (PSA). In general, the efficiency of a PSA is around 80%. The typical hydrogen purity after the PSA is 99.999 vol. %. In a PSA system, all remaining impurities of the hydrogen are removed in the adsorption bed. The tail gas from the PSA, which contains all the contaminants removed as well as some hydrogen, is used as fuel gas for the reformer burner. In general, 0.45 m^3 CH_4 per m^3 H_2 generated is required for the high-temperature steam reforming process.

High-temperature steam reforming is high in investment and low in utility costs (**figure 4**). This process is typically used for production capacities ***from 200 to over 100 000 m³/h H₂***.

Advanced hydrogen supply

Low-temperature steam reforming. The low-temperature steam reforming process ***(HCE Ultra process)*** is a more economical process for on-site production of hydrogen for demands of up to 300 m^3/h. A simplified flow sheet of the HCE Ultra process is shown in **figure 5**.

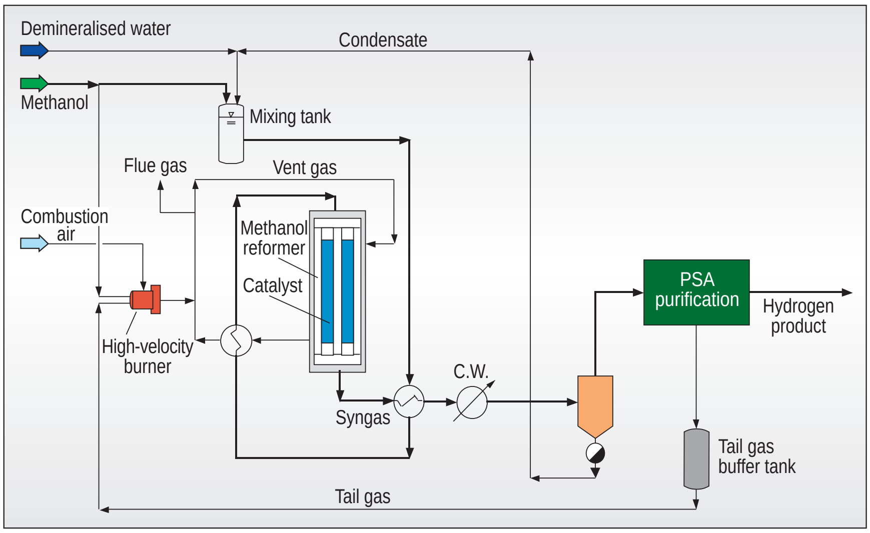

Figure 1. Methanol reforming process using a pressure swing adsorption unit

Figure 2. Methanol reforming plant with a capacity of 500 m^3/h hydrogen supply

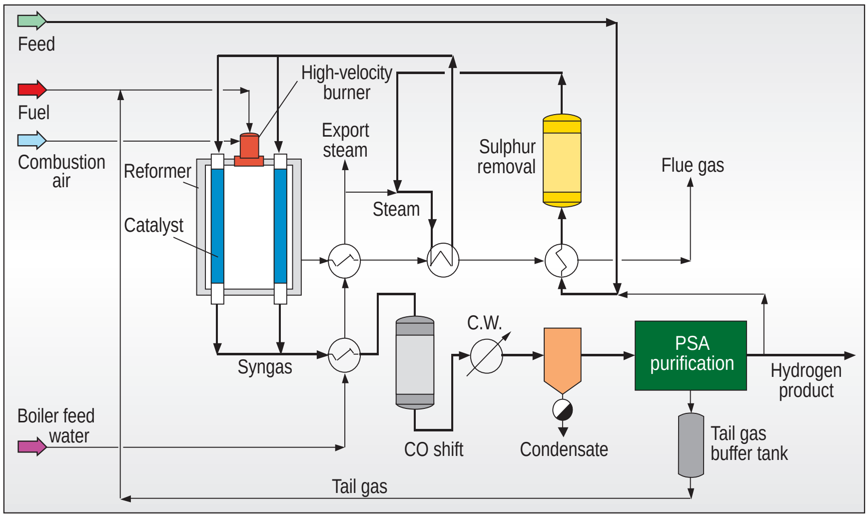

Figure 3. High temperature steam reforming process (HC)

Figure 4. HC steam reforming plant with a capacity of 500 m^3/h hydrogen supply

In ***only one conversion step*** a hydrogen-rich synthesis gas is produced at operating temperatures between 400 to max. 600 °C. The operating temperature depends on the type of feed used. The process described has significant advantages. Since it operates at significantly lower temperatures than a conventional steam reformer, the reformer tubing does not have to be made of high-temperature resistant alloys, but of less expensive materials. Furthermore, the reforming step is operated at nearly atmospheric pressure, i.e. below 1.5 bar. This results in an additional cost reduction in materials and engineering as well as in costs for approval and maintenance, since the reforming section is not subject to the European Pressure Equipment Directive (PED) 97/23/EC.

Since ***only small amounts of steam*** are required, it is beneficial to operate this process with import steam, which is usually available on site. In this case, there is no requirement for an internal steam generator. This means a cost reduction, not only because no waste heat boiler is required, but because no maintenance and supervision efforts are needed for this process step.

If import steam is not available on site, a standard packaged steam generator can be installed and operated. As the operating pressure of the reformer is close to atmospheric, the required steam pressure is also nearly atmospheric. Due to this fact, a packaged steam generator with design approval is both a suitable and economical solution.

Compared to the conventional steam reformer, the low-temperature steam reformer does ***not require a CO shift***, since the CO content of the synthesis gas produced is low due to the thermal equilibrium.

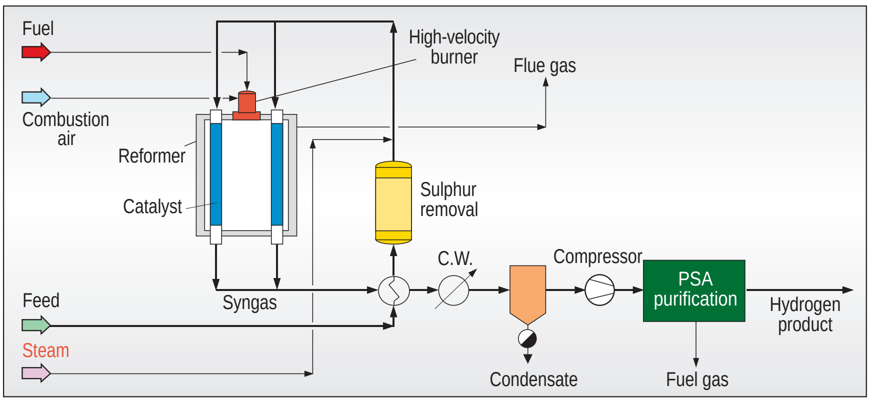

Figure 5. Low temperature steam reforming process (HCEU)

With high-temperature steam reforming, the tail gas coming from the PSA does not cover the total heat demand of the reformer. Therefore, additional natural gas has to be used as fuel. Due to the thermal equilibrium, the tail gas in the low-temperature steam reforming process provides excessive heat which can be exported as fuel gas. This process alternative results in a consumption of 0.38 m^3 CH_4 per m^3 H_2 produced.

Another advantage of the new HCE Ultra process is the choice of possible feed stock for the reformer. ***Natural gas, LPG or methanol*** can be used. One feed stock can be easily substituted for another, enabling fast reaction to changing market situations in terms of price and availability. In case of changing the feed, no changes to the reformer or to downstream units are necessary.

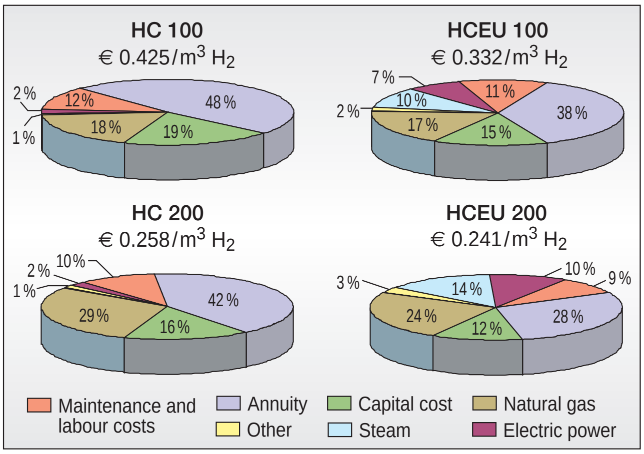

Figure 6. Production costs for hydrogen demands of 100 vs. 200 m^3/h, HC compared with HCEU process

The operating mode of the HCE Ultra process is fully automatic and nearly unmanned. Only for routine checks, from time to time a supervision is recommended.

The low-temperature steam reforming process is low in investment cost and low to moderate in utility cost. The typical range of this application is from 50 to 300 m^3/h H_2.

Production costs

The cost of hydrogen supplied ***by trailers*** are determined by the cost of transportation and typically vary between 0.3 and 0.5 €/m^3. With decreasing plant capacity, however, the costs for utilities and energy become less significant, whereas the costs of depreciation and interest on the investment become dominant factors. In order to produce small amounts of hydrogen economically, it is therefore essential to cut the investment of such on-site plants.

Figure 6 shows the distribution of the production costs for different hydrogen demands, i.e. 100 m^3/h and 200 m^3/h. HC is the abbreviation for the conventional steam reforming process shown in **figure 3** and HCEU for the low-temperature steam reforming process shown in **figure 5**. The calculations were made on the basis of the expenses listed in **table 1**. It was assumed that the projects are executed on a turn-key basis.

For a hydrogen ***demand of 100 m³/h***, there is a significant difference in production costs between HC and HCEU, which is estimated at € 0.093 per m^3 H_2. This adds up to possible cost savings of € 79 050/year. This cost reduction is achieved by cutting investment costs. The share of annuity and capital costs was decreased from 67% to 52%.

In case of a ***200 m³/h*** hydrogen generator, the difference in production costs is only minor. However, this break-even point may shift with changing utility costs or variations in annuity.

Table 1. Production costs for on-site hydrogen

Utilities	
Natural gas	0.15 €/m^3
Import steam	0.02 €/kg
Electric energy	0.06 €/kWh
Demineralized water	0.60 €/m^3
Cooling water	0.05 €/m^3
Services	
Operating time	8500 h/year
Annuity	10 years
Interest rate	8%
Maintenance (spare parts)	2% of plant investment per year
Personnel (labour costs)	15 000 €/year

In addition to the calculated production costs, the focus should not only be on the reliability of the hydrogen generator proper. It is often more important to take into consideration the ***general operating conditions*** of the plant into which the hydrogen generator is to be integrated, especially in the case of a batch-type operation. Here, the low-temperature steam reformer offers additional advantages (i.e. low temperatures and pressures), as this makes it insensitive to frequent start-ups and shut-downs.

The on-site hydrogen generation using the HCE Ultra process enables an ***advanced and fully automatic*** $\boldsymbol{H_2}$ ***supply***. This process requires only a minimum of investment costs and is therefore an economically attractive solution. ■