

DRIVING HYDROGEN EFFICIENCY WITH AN EYE ON THE ENVIRONMENT

Sanjiv Ratan, Technip, USA, and Nitin Patel and Bill Baade, Air Products, USA, provide details on the progression of hydrogen generation efficiency and reduced environmental impact.

The hydrogen alliance between Air Products and Technip was initiated in the early 1990s, also coinciding with the beginning of the Clean Fuels legislation in California and addressing of refiners' desire to outsource the hydrogen supply responsibility and capital in a low margin economic environment. The same underlying drivers are now becoming valid globally. This trend setting alliance has combined the two companies' strengths in the sale of gas (SOG) and sale of equipment (SOE) respectively. Over the years, on-purpose hydrogen needs have grown substantially due to three factors (Figure 1):

- Clean fuels moving to ultra low sulfur (ULS) specifications.
- Increased use of heavy, sour crude.
- Economic growth leading to increased demand for transport fuels.



Outsourcing of hydrogen supply grew substantially from a humble 100 million ft³/d, or 110 000 m³/h, to over 5.5 billion ft³/d or 6 million m³/h for refiners and chemical industries globally. On-purpose hydrogen became the lifeblood of a profitable, highly complex refinery producing significant volumes of clean fuels, for which the global marketplace continues to compete in current times and also potentially in the future. Air Products' current hydrogen forecast calls for an additional demand for 8 billion ft³/d (8.8 million m³/h) to be awarded and onstream by 2020. The hydrogen market will be more globally distributed over the next decade due to the three factors mentioned earlier and with the emergence of a new driver: replacement of ageing assets with high efficiency, state of the art hydrogen plants that also meet the new tougher environmental standards.

This article provides an outline of a selection of hydrogen plants built under the Air Products/Technip (AP-TP) H₂ alliance, beginning with the first one started up in 1994 through to one to be started up in 2012. The technical descriptions focus on the evolution of the SMR flowsheet towards improved efficiency, adaptation to refiners' evolving needs for power and steam (cogen) and multiple feedstocks (RFG, ROG, propane, butane and naphtha). An overview of the technology map provides a timeline of the developments in H₂ plant design (Figure 2).

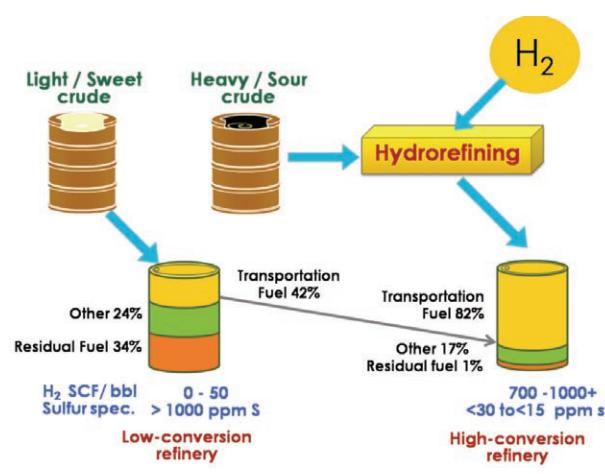


Figure 1. Refinery hydrogen growth.

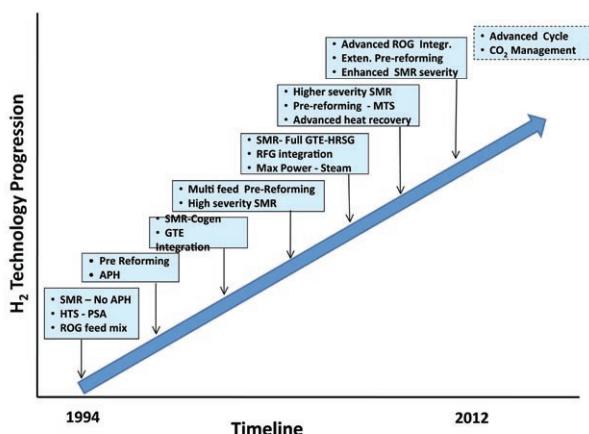


Figure 2. Hydrogen technology map.

Preface

From the beginning of the AP-TP H₂ alliance in 1992, the two companies have offered refiners a high efficiency H₂ plant based on steam methane reforming (SMR) technology with the then latest flow sheet involving high temperature shift (HTS) and pressure swing adsorption (PSA) for purification to a H₂ product purity of >99.99 vol.%. The higher H₂ purity fed to high pressure hydrotreaters and hydrocrackers provided refiners the opportunity to increase the H₂ partial pressure and the recycle stream purity resulting in lower purge stream volumes, higher unit conversion levels and extended hydroprocessing unit turnaround cycle times. The plants offered high efficiency by coproducing a large quantity of high pressure steam (>600 psig) for export to the refinery.

With an eye towards the environment, the initial six plants were constructed in California and Texas with selective catalytic reduction (SCR) units to achieve ultra low NO_x emissions levels, even though they were not required as of the startup date (some air permits would have allowed the use of low NO_x burners). Air Products published a paper in 1996¹ highlighting different NO_x emissions results from a number of different operating H₂ plants. The company shared new or extended correlations derived from plant test data with the hydrocarbon industry on predicting NO_x emissions including a traditional flowsheet H₂ plant and a newer high efficiency (air preheat) based SMR H₂ PSA plant. One significant conclusion was that a high efficiency SMR plant produces lower NO_x emissions due to the lower adiabatic flame temperature in the furnace resulting from the use of CO₂ rich PSA purge gas/NG blend versus a 100% NG fuel stream used in the conventional flowsheet SMR. Test results were significantly different than the predictions available at the time using the EPA's standard publication (AP-42 mostly based on boiler data)² for the design basis for the air permit for an SMR furnace, which allowed for a push towards higher efficiencies in future designs.

Over the past 17 years, the AP-TP alliance has realised over 30 hydrogen plants totalling a capacity of more than 2.3 billion ft³/d H₂, and has continually innovated the SMR flowsheet to incorporate new

Table 1. Heat recycle impact on CO₂

Grade of recycled heat	Process concept/option	Extent of application	Contribution to CO ₂ reduction
Low level	Combustion air preheating	Frequent	Large
Medium level	Prereforming	Moderate	Medium
High level	Post reforming	Selective	Fair

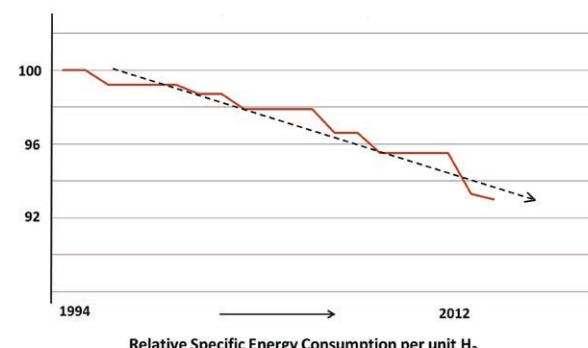


Figure 3. Hydrogen plant energy efficiency improvement over two decades.

technology developments and drive to increase efficiency (Figure 3), which has also lowered CO₂ emissions.

Hydrogen generation energy efficiency

Hydrogen production is inherently quite energy intensive, thus enhancing its overall efficiency is essential for improving its economics as well as environmental performance. For processing light hydrocarbon feedstocks, steam reforming is the technology of choice.

In a steam reforming hydrogen plant, the main thermal inefficiencies relate to:

Incomplete (low level) heat recovery from the process stream, which otherwise becomes uneconomical to recover, leading to substantial cooling duty.

Incomplete waste heat recovery from combustion in terms of loss in stack gas.

Incomplete conversion in terms of CH₄ and CO slip, resulting in higher feed flow, and thereby also increased sensible heat demand.

Incomplete H₂ recovery in PSA based plants (10 - 15% H₂ loss to purge gas fuel) or additional heat required for CO₂ removal in 'conventional' older plants, obtained partly via condensing duty from higher steam:carbon (S:C) ratios in reforming.

Heat loss to ambient.

Xergy losses in compression, if applied.

The following advanced technological design features have been incorporated in modern hydrogen plants by the AP-TP alliance for improving net energy efficiencies, while also enhancing their reliability and HSE aspects:

Extended heat recovery 'below the pinch' and its internal recycle.

Incorporation of more efficient process cycles based on reduced S:C ratios and higher severity.

Shifting involuntary steam generation (with high combustion air preheat and richer fuel after CO₂ recovery).

Cost effective exploitation of advanced steam power synergy and increased energy integration for enhancing the overall energy efficiencies and related CO₂ footprint.

Design optimisation

Further, steam reformer designs have been constantly adapted to satisfy the emerging needs for improved energy efficiency, cost effectiveness and environmental compliance. Major technology advancements in catalysts and tube metallurgy have allowed increased reforming severity, higher combustion air preheat, increased average heat flux, ultra low NO_x burners and reduced losses. Further, the mechanical design enhancements have been made possible through the capabilities of modern fast computers with rigorous simulation and computational tools, which include computational fluid dynamics (CFD) modelling and the 'hot system' advanced stress analysis, which also assist in predicting actual operational behaviours for ensuring uniformity of flow, heat and temperature for long term integrity and performance optimisation.

In comparison, a modern state of the art reformer is capable of providing up to 10 - 20% more capacity and more than 5% higher energy efficiency when compared to the same reformer of the early 1990s, while also carrying enhanced reliability and operational flexibility.

The alliance has been the forerunner in the application and integration of prereforming technology, with more than 40 units to Technip's credit. Air Products was the first gas supply company to apply it in the large hydrogen plant on multiple feedstocks at Tarragona, Spain, which started up in 2002.

Each hydrogen plant design is usually optimised through evaluation of several cases for the flow sheet optimisation in terms of selecting the process route and steps, followed by optimisation of the operating conditions and process variables for the selected flowsheet. To conduct such an exercise effectively, the following reliable information is required for the specific plant in question:

Unit price of feed, fuel and power.

Credit (and limit) of export steam.

Economic payback criteria for incremental investment.

Catalysts

The hydrogen process based on steam reforming is strongly driven and governed by the catalytic steps. Hence, proper selection and performance of catalysts play an intrinsically important role in optimisation and reliability of the process. Also the feedstock flexibility of steam reforming has been widely increased with the application of the prereforming step upstream from the reformer. Notable improvements have been made in the catalysts applied in hydrogen/syngas plants, mainly to respond to the sought after needs and desired characteristics that include:

Higher space velocities.

Higher resistance to poisons and process upsets.

Longer operating life leading to lower 'life cycle costs.'

Catalyst shapes for higher activity and lower pressure drop.

Easier loading, startup and reduction requirements.

Better selectivity/conversion (reduced formation of undesired byproducts).

Heat recycle

Recovering and recycling various levels of heat within an H₂ plant enables a reduction of the amount of fuel consumed by the SMR furnace, which in turn curtails CO₂ emission. In recent years, the H₂ alliance teams have designed and applied various such advanced concepts, which are broadly categorised in Table 1.

Refinery offgas integration

Burning H₂ containing refinery off gases (ROG) via the refinery fuel gas network at times can limit refinery capacity due to overall emissions limits (NO_x) and can impact the refinery economics. Based on proper integrated utilisation of such off gases, it can offer improved efficiency as well as cost effectiveness of the H₂ plants.

Various ROG integration options have been applied and proven based on their available pressure and H₂ contribution (volume * H₂ fraction). Further, a major link exists between H₂ and CO₂; management is through integration of refinery off gases (ROG) in the H₂ generation plant in order to exploit their H₂ content. There are various modes of such integration based on the achievable percentage of contribution from the ROG towards the desired H₂ generation capacity. Such integration also has implications towards the CO₂ balance, since the calorific value of the recovered H₂ must be eventually replaced by hydrocarbon fuel for the overall refinery fuel balance. However, the net result is quite favorable for the overall refinery carbon footprint.

Captive steam power synergy

With a typical modern hydrogen plant being a net exporter of steam, cogeneration of power from this steam can represent a higher value end use and can prove quite attractive under certain fuel power scenario and for locations having insufficient or unreliable grid power supply. Also for grassroots refineries, major expansions or upgrading projects requiring substantial captive power and steam, integrating a gas turbine (GT) combined cycle in a fairly large size (>80 000 m³/h)



Figure 4. Repsol, Spain, H₂ plant with partial CO₂ capture.



Figure 5. Port Arthur 2, Texas, H₂ plant with combined cycle.

hydrogen plant can also prove to improve overall integration economics as well as to lower the equivalent CO₂.

The GT exhaust can be partly integrated as hot combustion air for the reformer furnace and the rest can be sent to heat recovery steam generation (HRSG) for extended steam power synergy. In such a configuration, a 30 MW GT can be integrated into a 100 000 m³/h H₂ plant providing up to 75 MW based on combined cycle as well as export steam. Such an integrated H₂ steam power plant can lower the equivalent CO₂ by 15 - 20% when compared to stand alone individual units and has been well proven in some of the large modern hydrogen plants.

Most hydrogen plants can be configured to coproduce various amounts of byproducts, such as high and low steam, electric power, and/or carbon oxides. The following brief case studies highlight AP-TP H₂ alliance's value added concepts and different process design integrations that were successfully demonstrated in a variety of refinery hydrogen projects over the past two decades.

Advanced process control

Hydrogen plant process control has evolved over the years to modern, fully automatic integrated DCS systems, also involving complex multi variable control and online plant optimisation. This advancement has led to improved efficiency, reliability, safety and ease of operation. The advanced plant control systems often use specific diagnostic routines as well as simulation models and algorithms for plant optimisation and parametric control. They can conduct direct data reconciliation and multi variable sensitivity analysis based on time based measured data. Further, they can be equipped with a functional decision support system for providing optimised external set points against a defined objective function or operational targets (best feed for minimum operating cost or maximised hydrogen production etc.) Also in a multiple feed based plant, automatic feedstock, changeover systems are often desired/employed, which provide smooth, faster and reliable feed changeover

flexibility by avoiding operator induced errors as well as any step reduction in the production.

Selective reference hydrogen plants

Martinez, California, USA, H₂ plants (1994 - 95)

These two hydrogen plants were tailored to accommodate the needs of the two refineries in the area, in terms of their hydrogen and steam requirements, and the utilisation of the refinery fuel gas (RFG) streams by Air Products. One plant was designed to maximise hydrogen generation efficiency while at the same time minimising export steam to the refinery. The other was custom designed to process a blend of up to eight different RFG streams to be used as either feed or fuel to the reformer.

Both these plants were based on SMR technology involving both high and low temperature shift reactors, and a PSA for final purification of the hydrogen product stream. The plants' control systems were designed accordingly, for the first plant to minimise the export steam generation, and for the other one to minimise the effects of varying blended RFG feed and fuel compositions to the reformer on hydrogen and steam product quality. These plants produced 35 and 88.5 million ft³/d (38 000 m³/h and 97 000 m³/h) of high purity hydrogen, respectively, to serve two large refineries in the Martinez, CA, area. In addition, both these plants also meet strict environmental regulations at respective sites, which included low NO_x reformer burners, SCR unit, and continuous emission monitoring system (CEMS).

Repsol/Tarragona, Spain (2002)

This was the first large (approximately 60 million ft³/d (67 000 m³/h) hydrogen plant built by Air Products Europe and Technip Benelux in Spain. The plant design was rated for an additional capacity with limited investment in key critical equipment. The facility also coproduces 200 tpd of food grade liquid CO₂ for export. The plant incorporates a prereformer, primary reformer, 10 beds PSA, and an aMDEA CO₂ recovery system. In addition to normal natural gas feed and fuel to the reformer, the plant is also capable of processing naphtha as well as refinery fuel gas as reformer feed and fuel respectively when requested by the refinery. The prereformer was designed (mechanically), and optimised (operationally) to accommodate both the natural gas and naphtha processing.

Port Arthur 2, Texas, USA (2006)

This was the second large hydrogen plant located at Valero's Port Arthur, Texas, USA, refinery. The plant is designed to produce 110 million ft³/d (123 000 m³/h) of high purity hydrogen product for Valero, and is also integrated with a CGT. A portion of the CGT exhaust is ducted to the reformer furnace as preheated combustion air, and the remaining exhaust is sent to heat recovery steam generation (HRSG). The HRSG is designed for RFG firing to maximise steam generation when needed. This facility, in addition to hydrogen, also produces up to 540 tph of high pressure steam, and 100 MW of electric power.

This plant also includes a 20 MW back pressure steam turbine to provide flexibility to refinery demand for high and low pressure steam as well as hydrogen production rate.

Edmonton 2, Canada (2008)

This is the most modern hydrogen plant operated to date with a capacity of 105 million ft³/d (115 000 m³/h) H₂, with high export steam. There is no power cogeneration at this site. The plant provides hydrogen to the refinery to produce cleaner transportation fuels and other products from processing of Canadian oilsands synthetic crude.

Figure 6. Suncor Edmonton 2, Canada high efficiency H₂ plant.



This plant serves Suncor (formerly Petro-Canada) and Imperial Oil Refineries in Alberta. The plant flow sheet includes operation at an aggressively low S:C ratio in the reformer, with a prereformer and medium temperature shift (MTS) technologies integrated to the overall process for heat integration to achieve high specific efficiency.

Rotterdam, the Netherlands (2012)

This 120 million ft³/d (134 000 m³/h) plant is currently in the design phase. It is designed to process low pressure and high pressure RFG streams, and natural gas in the reformer. The hydrogenation of olefins in the RFG streams is optimised by controlling the mixture of RFGs and natural gas to the hydrogenator reactor. In addition to the prereformer, low S:C and MTS technologies, to further lower energy consumption, this plant incorporates some of the advanced technological design features of extended heat recovery and its internal recycle, as well as low level heat integration.

Future high efficiency hydrogen plant

Carrying on with the continuous improvement programme and product line technology development, the AP-TP alliance teams continue to work towards developing a hydrogen plant of the future, having still higher energy efficiency, while staying cost effective and retaining the highest standards of safety and reliability. With the targets of further harnessing residual energy losses and thermodynamic inefficiencies, the endeavor includes pilot testing, catalyst alignment and other concerted R&D efforts in order to ensure its required demonstration and eventual implementation, offering a reduced carbon footprint.

Conclusions

It is well acknowledged that a hydrogen plant constitutes a substantial part of the energy input, costs and environmental impact in a refinery. Thus, it carries a strong drive and concerted strife for improving its SMR energy efficiency, with the added objective of subsequently reducing GHG emissions and lowering a refinery's future CO₂ footprint. This is especially relevant when considering replacing ageing SMR assets (1960s -1970s refinery SMRs). Realising that in a deep conversion refinery, the CO₂ release from its hydrogen plant (SMR) could be up to 25% of a refinery's

total CO₂ emissions, the technological advancements and continuous improvement efforts are able to appreciably reduce the energy consumption and thereby the related CO₂ footprint partly by shifting it elsewhere for more effective centralised CO₂ capture in future.

Over the successful tenure of 17 years of the AP-TP hydrogen alliance, the technology advancement and development efforts have been largely focused on enhancing the hydrogen generation efficiency as well as reliability in a cost effective manner, while maintaining the highest HSE standards. Such deliberations have yielded an energy efficiency improvement of 5 - 7% from an already high threshold, involving integration of advanced heat recovery and heat recycle concepts. It coincidentally also offers CO₂ curtailment/avoidance potential of 25 - 40% by minimising involuntary export steam and switching to centralised steam power facility with imminent carbon capture capability, thus allowing timely readiness for the future environmental challenges. ■

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