

High times for HYDROGEN

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look at the continuing growth in hydrogen capacity for the production of clean fuels.



Hydrogen has been an integral component of the majority of refinery clean fuels projects since the first wave emerged in California in the early 1990s. As the waves of clean fuels regulations migrated across the entire USA, Canada and Western Europe, some refineries incorporated economic expansions into their projects in order to provide a return on the total investment. In addition, some refiners shifted their feedstock to heavier, more sour crudes to provide an additional economic driver. The combination of three major trends over the past 12 years has led to a significant growth in new hydrogen capacity. Air Products has led the way towards outsourcing of hydrogen supply to refiners with a combination of different technological solutions tailored to individual refiner's needs.

Outsourcing of hydrogen to both refiners and chemical producers has grown from a small base of capacity in 1991 of less than 240 tpd (100 MMSCFD) to over 11 000 tpd (4600 MMSCFD) in 2006. Air Products has 4800 tpd (2000 MMSCFD) of H₂ capacity currently operating and plants under construction. There are numerous reasons refiners have elected to outsource their hydrogen supply, including access to multiple sourced hydrogen pipelines, access to industrial gas, suppliers' depth of recent hydrogen plant project experience, and a focus on integrating lessons learned into operational

reliability enhancements for their next plant design. Over the next 12 years, Air Products hydrogen plants increased in both size and scope to address specific needs of refiners. The following brief case studies will highlight some value added concepts and integration of technologies successfully utilised in a variety of refinery hydrogen projects since 1994.

Case studies

- Martinez 1, California (1993). This plant was designed as an expandable 60 tpd (25 MMSCFD) hydrogen plant to meet the customer's future demand. It currently operates at over 140% of the original design capacity with increased hydrogen product reliability. This plant was also designed to provide feedstock flexibility (natural gas, LPG, and/or butane), limit export steam generation, and meet strict environmental regulations at the site, including a selective catalytic reduction (SCR) system.
- Pernis, the Netherlands (1994). This is the largest Air Products' H₂/CO co-production facility in Europe, and was originally a mid 1960s M.W. Kellogg 1000 tpd ammonia plant. It was successfully debottlenecked and converted to produce hydrogen and carbon monoxide. For overall cost effective conversion, the air secondary reformer/MEA units were bypassed, and PSA/VSA units were



Figure 1. The Martinez 2 hydrogen production facility.



Figure 2. Air Products' hydrogen production facility in Tarragona, Spain.



Figure 3. The hydrogen production facility at Convent, Louisiana.

added to produce high purity streams of hydrogen and carbon monoxide products. The existing steam turbines in the plant were converted to generate electric power for internal consumption and export to the grid.

Refineries produce a wide range of hydrocarbons with the potential to be used as feedstocks to a hydrogen plant. Therefore the selection of the appropriate feedstock and technology for a specific application requires a detailed analysis to determine which combination provides the lowest cost hydrogen. These next two examples illustrate different methods of integration with the hydrogen plant to add value to refiner's operations.

- Martinez 2, California (1995). This hydrogen plant was

designed to process a blend of up to eight different refinery fuel gas (RFG) streams from Shell's Martinez refinery to be used as either feed or fuel to the reformer. The plant is custom designed to accommodate these multiple feeds and fuel streams to produce 212 tpd (88 MMSCFD) of high purity hydrogen at 140 barg (2000 psig) and superheated steam for export. The plant control system was designed to minimise the effects of varying feed and fuel compositions on hydrogen and steam product quality.

- Wilmington, California (1996). A 193 tpd (80 MMSCFD) hydrogen plant was designed to process RFG streams, containing some olefins as reformer feed and fuel. The plant generates 103 barg (1500 psig), high pressure superheated steam and is integrated with a 32 MW condensing turbine. The condensing turbine includes two steam extraction nozzles, a medium pressure for process use and a low pressure for export. This plant supplies electric power for internal use in the refinery and/or export to the grid. In addition, it also incorporates Air Products' 'utilities centre' concept to gain the economies of scale in providing utilities for both the H₂ plant and the refinery CARB fuels project.

In this next case, Air Products drove to a lower cost solution for hydrogen production on its pipeline network in Houston, Texas, by economies of scale and integrating the needs of its chemical customers with its refinery customers.

- LaPorte HyCO 3, Texas (1996). This 156.5 tpd (65 MMSCFD) hydrogen plus carbon monoxide (CO) and syngas plant was primarily designed to supply pure CO product to a nearby acetic acid plant, and hydrogen fed to Air Products' Texas pipeline supplying various refineries and petrochemical facilities. The plant includes a dual train GE partial oxidation (POX) of natural gas, MEA CO₂ removal unit, and a partial condensation cold box.

Air Products commissioned two hydrogen plants early in the decade to supply hydrogen for their hydrocracking requirements, which incorporated two different approaches to adding value to their refining operations.

- Port Arthur, Texas (2000). This 241 tpd (100 MMSCFD) hydrogen plant is integrated with a combustion gas turbine (CGT) to coproduce and export electric power, high pressure steam and hydrogen to the adjacent refinery. The CGT exhaust is ducted to the reformer furnace as preheated combustion air to improve the overall operating efficiency and reduce capital cost. The plant is designed and successfully operates either independently or in integrated mode to enhance reliability of the facility.
- Tarragona, Spain (2002). The first large 144.5 tpd (60 MMSCFD) hydrogen plant built by Air Products' Europe and Technip Benelux is in Spain and serves the Repsol refinery. The plant design was rated for an additional capacity with limited pre-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, multi-bed PSA, and an MDEA CO₂ recovery system.

Air Products has a strategic focus on hydrogen as a corporate 'growth platform'. Therefore, the company has a significant R&D programme to evaluate and test new technologies and implement them in the plants as they are ready for commercialisation. Two recent examples are



Figure 4. The Sarnia SMR plant in Ontario, Canada.



Figure 5. Aerial view of Port Arthur 1 and 2.

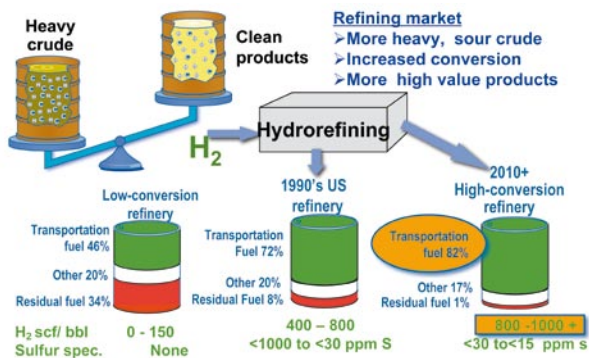


Figure 6. Why the high growth? Hydrogen intensity is increasing to meet global demand for transport fuels.

highlighted in the following hydrogen plants.


- New Orleans (NOLA D), Louisiana (2003). This 96.3 tpd (40 MMSCFD) hydrogen plant includes Air Products' in-house developed enhanced heat transfer reformer (EHTR), to manage reformer waste heat steam generation. The EHTR reactor, located downstream of the primary reformer, utilises the hot reformer effluent stream to reform a portion of the incoming hydrocarbon feed stream, instead of a process gas boiler. This plant has zero export steam.
- Westlake, Louisiana (2004). This is a modern hydrogen plant design with a capacity, to date, in excess of 241 tpd (100 MMSCFD) H₂, with export steam. The plant design includes Air Products' in-house developed large scale vortex (LSV) burners, which enables the primary flame to operate at ultra lean conditions for low NO_x

emissions operation.

Recently, Air Products has brought onstream two hydrogen projects in Canada for clean fuels at the Shell/Sarnia and Petro-Canada/Edmonton refineries.

- Edmonton, Alberta (2006). This is the most modern hydrogen plant design to date with a capacity in excess of 168 tpd (70 MMSCFD) H₂, with export steam. The plant serves PetroCanada and Imperial Oil refineries. The plant provides hydrogen to the refineries to produce cleaner transportation fuels and other products from heavier, sour crude feedstocks. Additionally, Air Products is currently engineering for construction of a second hydrogen plant with a capacity of 253 tpd (105 MMSCFD) for the processing of Canadian oilsands crude, which is expected to come onstream in April 2008.
- Sarnia, Ontario (2006). This hydrogen plant has a capacity in excess of 192.6 tpd (80 MMSCFD) H₂, with export steam and is integrated with Air Products' Canada liquid hydrogen facility in Sarnia. The plant serves refineries owned by Shell Canada Products and Suncor Energy Products. The plant is located at the Shell refinery and also provides hydrogen via pipeline to the Suncor refinery. The refineries use the hydrogen to produce ultra low sulfur diesel and other clean transportation fuels.
- Convent, Louisiana, and Baytown, Texas (2006). These two hydrogen plants were in full construction during Autumn 2005 in the USGC. Despite some of the difficulties brought by the two hurricanes, the facilities were operational very close to their original schedule. The 265 tpd (110 MMSCFD) Convent plant serves the Motiva Enterprises LLC refinery and others along the Mississippi River corridor pipeline system, along a 90 mile pipeline network from Baton Rouge to Norco, Louisiana. The Baytown facility was expanded to provide 168.5 tpd (70 MMSCFD) hydrogen to the ExxonMobil refinery and others along the West Gulf Coast pipeline system extending from Houston, Texas, to Lake Charles, Louisiana. The facility continues to recover carbon monoxide and HyCO syngas for chemical users in addition to the hydrogen from ExxonMobil's Syngas facility, originally commissioned in 2000.
- Port Arthur 2, Texas (2006). This is the second large hydrogen plant located at Valero's Port Arthur refinery. This SMR is integrated with a much larger combustion gas turbine as well as a HRSG for additional steam and power production. The supply arrangement is one of over 30 that Air Products has undertaken with refiners worldwide. With the addition of the Port Arthur 2 facility, the combined USGC hydrogen pipeline systems exceeds 2167 tpd (900 MMSCFD) and over 500 miles of pipeline networks on a global basis.

Conclusion

Refiners continue to face challenges in reconfiguring their refineries as they enter the ultra clean fuels era at a time when demand for increased transportation fuels is growing at high rates, globally. Grassroots refineries in the USA, Middle East, China and India are being announced to serve this projected growth in demand as regional and global refinery utilisation rates are at record high levels. Major refinery expansions and continued heavy, sour crude feed flexibility refinery projects are also being discussed for the next 5 - 10 years. Hydrogen intensity for refineries is anticipated to continue to increase, as illustrated by Figure 6. 



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