HYDROCARBON ENGINEERING

Integrated gas supply

G.H. Shahani and R.C. Best, Air Products and Chemicals, Inc., USA, and S. Sekhri and M.P. Ralston, Technip, USA, discuss the market forces reshaping the worldwide refinery market and outline several options for the simultaneous supply of hydrogen, oxygen, nitrogen and utilities.

The refining industry was impacted on several fronts in the 1990s. Firstly, environmental regulations became increasingly stringent. Additionally, in the aggregate, crude oil has become heavier and more sour. These effects have increased hydrogen demand. At the same time, refiners have had to increase sulfur removal, and in some cases, their catalytic cracking capacity. Both of these can be achieved by oxygen enrichment. Also, refiners have an ongoing need for nitrogen for blanketing and inerting. Furthermore, in today's competitive marketplace, refiners are outsourcing products and services to which the refiner does not directly add value. The confluence of these changes in the marketplace has brought about new opportunities for sourcing industrial gases such as H_2, O_2 and N_2, in an integrated manner from a single supplier.

The supply of industrial gases by third party specialists can be particularly valuable when these requirements become large enough to justify the development of a separate onsite supply infrastructure. Air Products has pioneered an innovative approach in which multiple products and services are produced, supplied and managed by an industrial gas company. By outsourcing all industrial gas needs to a single supplier, a refinery can focus its resources on its core business, thereby taking advantage of an industrial gas producer's expertise. The main advantages for refiners are:

- Integrated project execution.
- Economy of scale.
- Reduced plot space.
- Improved energy efficiency.
- Operations and maintenance synergy.
- Improved reliability.
- Superior environmental performance.
- Simplified contract management.

These factors translate into lower total cost and higher reliability for each of the industrial gases. Several options for exploiting the synergy in industrial gas supply will be reviewed.

Outsourcing trend

The trend to outsource non core activities is impacting almost every manufacturing sector on a worldwide basis. Initially, outsourcing of a certain function was selectively employed by smaller companies as a means of obtaining necessary expertise without making a large investment. The outsourcing philosophy is being embraced by the largest multinationals as a means of becoming more cost competitive. There is a growing recognition of the need to concentrate on core competencies in which a company can attain world class status. Activities that fall outside this realm are more advantageously outsourced. Examples of outsourcing range from plant security, landscaping, and cafeteria services to process plant engineering, design, construction and operation. In the context of industrial gases, outsourcing reduces cost, improves environmental performance and enhances reliability, which ultimately improves the refiner's profitability.

Market trends

Refiners are facing critical challenges in North America and Europe to produce clean motor transportation fuels by reconfiguring refinery processes with limited capital resources; all under the background of changing crude and product slates. Industrial gas suppliers can assist refiners by providing flexibility to their operations and improving their financial performance as measured by return on capital employed (ROCE).

Demand for H_2, O_2, and N_2 is expected to increase at both North American and European refineries over the

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However, in some cases the logistics of conveying steam to the use point and the refiner's supply/demand balances are such that it is better to minimise steam production. This can be achieved by expending capital in the H_2 plant design to bring about greater process heat integration. An alternative is to use the high pressure steam to drive the rotating machinery in the H_2 plant and the air separation unit including: main air compressor and product compressors in the ASU, cooling water pumps, boiler feed water pumps and induced draft/forced draft fans. Depending on the size of the air plant and the pressure of the gaseous products, this can be an excellent use of the by-product steam.

Alternatively, depending on the local demand for electric power, the H_2 plant can be integrated with a steam or gas turbine to produce electricity[1]

Compressed dry air and nitrogen

A hydrogen plant typically needs compressed dry air for a variety of plant uses including instrumentation and pneumatic valves. Gaseous nitrogen is used for inert flammable gases and liquids and it may also be used as a backup for instrument air. It is economical to produce and supply compressed air and nitrogen from the air separation plant. The alternative is to import and vaporise liquid nitrogen, which is more expensive.

Cooling water

The cooling water requirements for both the ASU and H_2 plant are significant. By building a single large cooling tower to serve the needs of both plants, it is possible to save on capital and operating costs.

Power supply

A single large power supply system for both the air separation and H_2 plant can provide savings in terms of initial capital cost. Design aspects and components such as the electric utility interface, switchgear, motor control centre and transformers can be common. Additionally, operating and maintenance costs and warehousing can be simplified. It is important to consider plant reliability and redundancy in designing this system.

Plot requirements

If the two projects are conceived and developed jointly, the total plot requirements will be reduced. Furthermore, arrangements for securing a land lease and paying property taxes will be simplified.

Control system

Both production processes require a central control and maintenance building with a climate controlled control room that contains the distributed control system (DCS), uninterrupted power supply (UPS), telecommunications equipment, other monitoring equipment and offices. Some of the equipment that can be common are the servers, computers, historians and operator interfaces. To the extent that a single consolidated control room can be designed and built, it is possible to realise savings in plot space. Office space can be shared and additionally, ongoing savings are possible by having a single operating team to oversee both production units.

Common spare parts

Spare parts for machinery, valves and instrumentation that are common between an air separation and H_2 plant can be shared. This leads to savings in capital costs.

Effluent, sewer and building permits

Environmental considerations are becoming increasingly important in most countries. It is essential to develop the appropriate environmental strategy and secure the necessary permits in a timely fashion so that the project schedule is not compromised. Applying for a single permit that covers both production processes minimises paperwork, application fees and consultant costs.

Project execution

By executing the air separation and hydrogen project simultaneously, savings in schedule and cost will be realised by streamlining the overall process. Project management and construction supervision costs can be shared.

Contract administration

For a customer, it is simpler and more efficient to deal with a single supplier for all the industrial gas needs. A single contract to cover multiple gaseous products and services can be developed. This approach enables the customer to deal with a single entity in developing the project scope, and subsequently through design, procurement and construction. Furthermore, once the plant becomes operational, the single point of contact remains in place. Such an approach facilitates quick response to the customer's needs and provides the foundation for a successful long term relationship.

Conclusion

A refiner's need for hydrogen, oxygen, nitrogen and utilities can be met cost effectively in an integrated manner from a single supplier. The main advantages are: integrated project execution, economy of scale, reduced plot space, improved energy efficiency, operations and maintenance synergy, improved reliability, superior environmental performance, and simplified contract management. These factors translate into lower total cost and higher reliability for the customer.

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Notes

*It may be noted that a catalytic reformer is the only major source of by-product hydrogen in a refinery.

The endothermic reaction in the tubes converts the hydrocarbon/steam mixture to hydrogen, carbon monoxide and carbon dioxide. Reformer effluent is sent to a shift reactor where most of the carbon monoxide reacts with steam and is further shifted to hydrogen. The gas is finally cooled and purified to produce H_2 product. Extensive heat integration in a steam methane reformer (SMR) ensures high energy efficiency[2].

Synergy between air separation and hydrogen plant

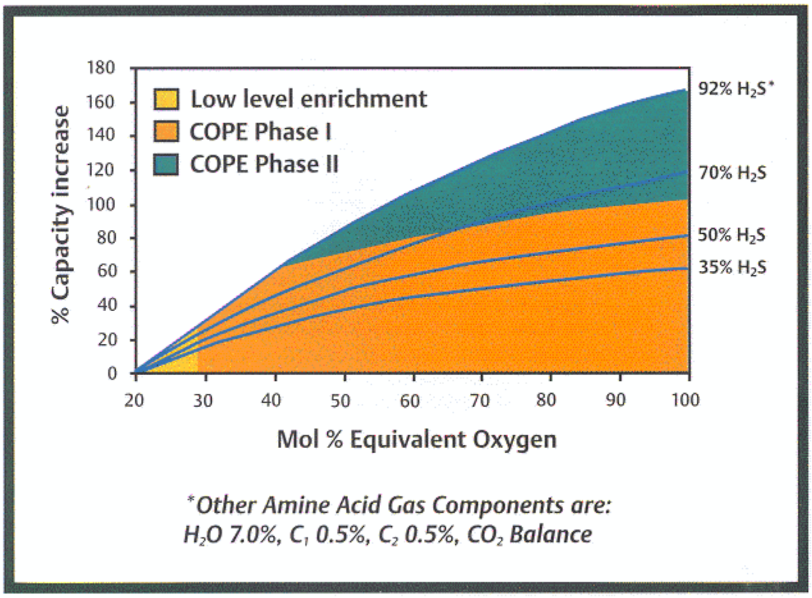
Some opportunities for integrating an air separation unit (ASU) and hydrogen production processes are described below, and presented in Figure 2. Cryogenic air separation employs physical separation at extremely low temperatures to bring about the distillation of air into its constituents. By contrast, hydrogen production by steam methane reforming is a high temperature, catalytic process employing heat transfer and adsorptive separation. However, there are similarities between the two production processes that lend themselves to process integration. Both are continuous processes that employ rotating machinery and sophisticated process controls. Furthermore, both processes are capital, energy and power intensive. The skills and knowledge required to develop a large process project, whether it is an ASU or H_2 plant, are similar. Both need careful evaluation of process cycles, by-product values and utility requirements in order to optimise total cost. Access to water, electricity and sewage discharge have to be considered for proper site selection. Furthermore, permitting, construction, start up and commissioning strategies have to be developed. Opportunities for synergy between air separation and hydrogen plants are discussed below.

Gasification

Gasification or partial oxidation (POX) is a non-catalytic process that has been successfully used to produce hydrogen, carbon monoxide and syngas. The process is carried out by reacting hydrocarbons, such as natural gas and oxygen, at elevated temperatures in a refractory lined vessel. Steam or carbon dioxide is used as a moderator, to fine tune the syngas composition. For example, while the H_2/CO ratio for unmoderated POX operation is between 1.7 - 1.9, this can be increased to over 2.5 by the addition of steam, or reduced down to 1.0 by recycling CO_2 into the feed. Since the process is non-catalytic, a wide choice of feedstock is possible. Commercial applications include feedstocks ranging from natural gas and butanes to vacuum resides and petroleum coke. In locations where oxygen cost is low, this process provides feedstock flexibility, high conversion, low NOx emissions, high pressure operation, and lower CO_2 in syngas. This process is also suitable for CO co-production. For gasification of natural gas, the oxygen requirement is 11 - 12 t/MMSCFD of H_2.

Secondary reforming

Steam methane reforming (SMR) followed by an oxygen blown secondary reformer is another proven process that utilises oxygen for syngas/hydrogen generation. For hydrogen production, this technology provides a cost effective means to expand an existing plant's capacity by up to 25 - 50%. The secondary reformer is installed downstream of the primary reformer and consists of a refractory lined vessel. The reactor, which is similar to the POX reactor, contains catalyst. The primary reformer effluent and oxygen is fed to the secondary reformer through a burner. Partial oxidation reactions occur in the top part of the vessel, above the catalyst. The mixture then passes through the catalyst bed where reforming reactions take place. Syngas from the secondary reformer exits between 1750 - 1900 ˚F. In debottlenecking applications, a portion of the reforming load is shifted from the primary to the secondary reformer. Feed flow to the primary reformer is increased and the outlet temperature is reduced in order to maintain the firing rate. To satisfy hydraulics, the steam to carbon ratio may also be reduced below design since the primary reformer operates at less severity. The resultant effluent has a higher methane slip, which gets converted in the secondary reformer. In locations where oxygen is available, this process offers the advantage of significant increase in hydrogen production without any increase in NOx emissions. For debottleneck applications, the oxygen requirement depends on various parameters such as the extent of capacity increase, as well as secondary reformer operating temperature. Typical oxygen requirements range between 10 - 20 t/MMSCF of H_2.



**Other Amine Acid Gas Components are: H_2O 7.0%, C_1 0.5%, C_2 0.5%, CO_2 Balance*

Figure 3. COPE™ capacity expansions in Claus sulfur recovery units.

Autothermal reforming

Autothermal reforming technology incorporates gasification as well as secondary reforming in one step. Feed hydrocarbon, process steam and oxygen is fed into a refractory lined vessel through a burner. Partial oxidation reactions take place in the combustion zone at the top of the reactor. The gas mixture then passes through the catalyst bed where reforming takes place. The reactor is very similar to a secondary reformer with a burner at the top head followed by a combustion section and catalyst bed. Process gas exits the autothermal reactor at ~1900 ˚F. Compared to gasification, the autothermal reformer provides a higher hydrogen to carbon monoxide ratio in the effluent.

Steam and/or power integration

Typically, a hydrogen plant produces steam as a by-product. In many instances, the refiner can use the by-product steam.

to 2750 - 2800 °F. Air Products and Goar Allison and Associates, Inc. (GAA) offer this technology; and the COPE™ burner is engineered and fabricated by L.D. Duiker b.V. in the Netherlands.

High level oxygen enrichment

High level oxygen enrichment, which entails O_2 enrichment over 40 - 50%, provides over 150% capacity increase for rich acid gas streams. In multiple sulfur recovery units, oxygen enrichment can provide 100% capacity redundancy. High levels of O_2 enrichment require special temperature moderation technology. Air Products' technology is known as the GAA/Air Products' COPE™ Phase II Process.

Fluid catalytic cracking

Many refiners have chosen to shift their refinery crude slate towards heavy, sour crude versus light sweet crude to improve margins. In the fluid catalytic cracking unit (FCC), the increased coke make, as measured by Conradson carbon number, imposes more stringent requirements on the regenerator air delivery system.

Low level oxygen enrichment (<28% O_2) of FCC regenerator combustion air has been safely practised for many years as a proven way to increase production rates in units that are limited by regenerator gas velocity or air blower capacity. A common problem in hot and humid weather is the reduction in FCC air blower output. Oxygen enrichment of 22 - 28% has allowed refiners to maintain their desired FCC output during the summer months. Oxygen can also be applied to solve a regenerator velocity limitation. This tends to be a continuous, year round application. A properly designed FCC enrichment program increases refinery profits by improving throughput and conversion.

Spent sulfuric acid regeneration

Spent acid regeneration (SAR) processes spent sulfuric acid from the alkylation process by first burning the spent acid to SO_2 in a furnace, followed by a downstream conversion to sulfuric acid. Oxygen is used in the SAR furnace to enrich the combustion air. This debottlenecks the furnace, thereby increasing spent acid processing capacity.

Wastewater treatment

Oxygen applied to a wastewater treatment system helps to increase capacity, produce cleaner effluent and reduce volatile emissions. Air Products provides an oxygen based wastewater treatment technology called OxyDep™ and has experience with providing oxygen and flow control equipment for this application.

Air separation and hydrogen production

Air separation

For almost a century, cryogenic air separation has been the dominant method for separating atmospheric gases. This technology can produce high purity oxygen (99.9%) at capacities from 20 to over 2000 tpd. Cryogenic air separation plants are particularly well suited for large capacity, continuous supply of high purity product.

Hydrogen production

Generation of on purpose hydrogen in refineries is achieved predominantly by steam reforming of hydrocarbons. In this process, a hydrocarbon feedstock, such as natural gas and steam, is mixed and preheated to approximately 1000 °F. The mixture is then sent to the reformer, which is a fired heater containing tubes filled with catalyst.

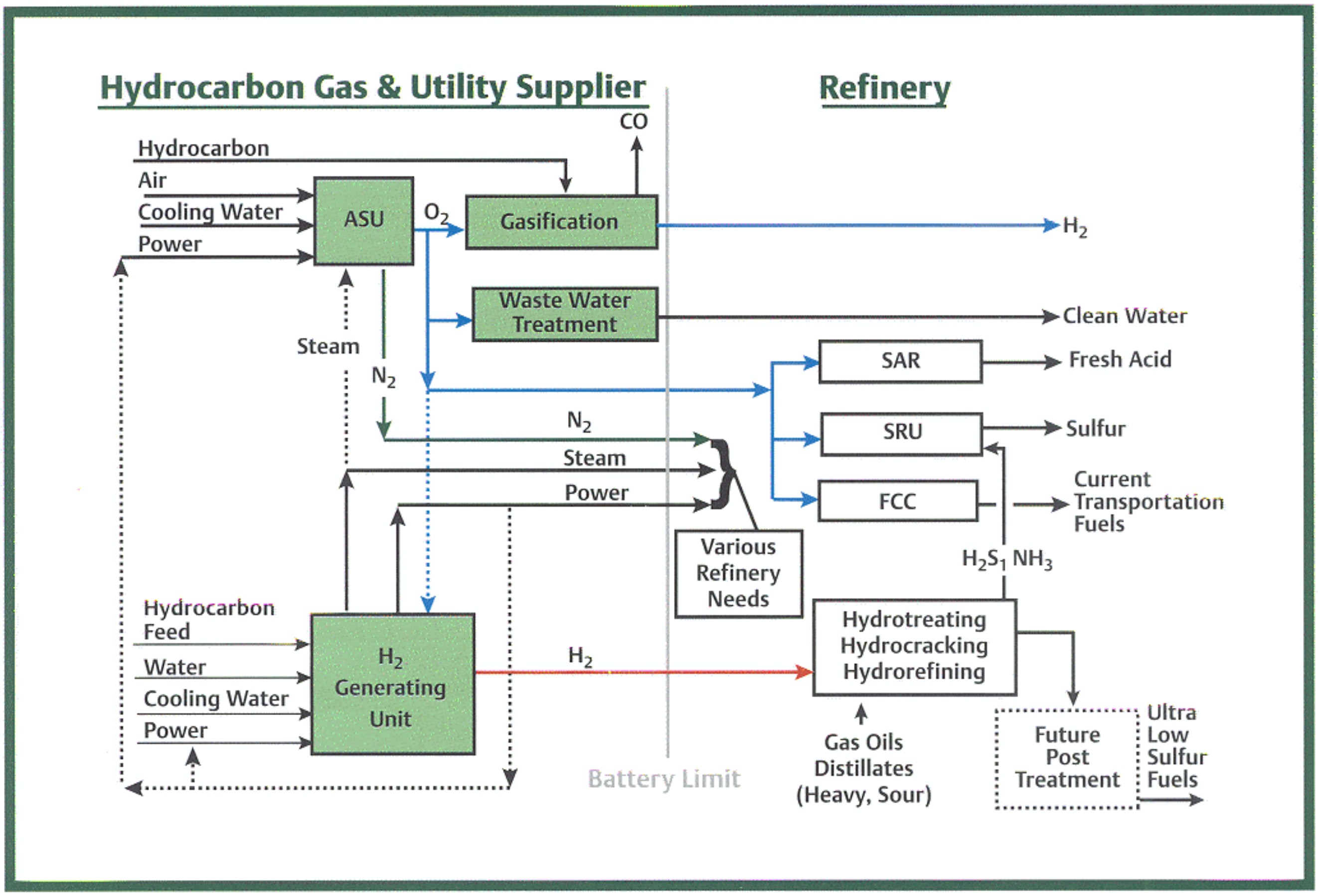


Figure 2. Integrated gas and utility supply.

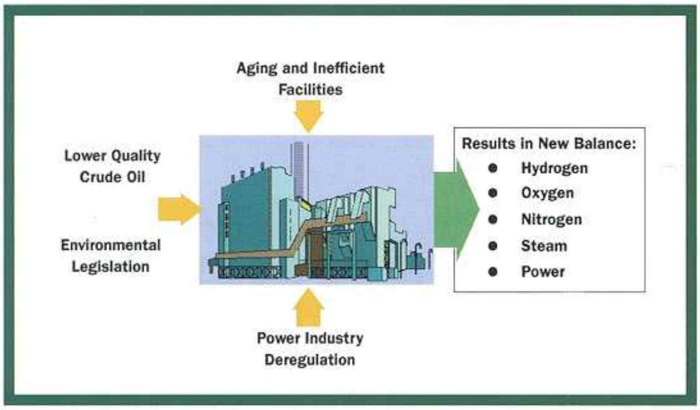


Figure 1. Forces impacting refiners.

next few years. The main factors driving this demand are depicted in Figure 1 and discussed below.

Lower quality crude oil

Crude oil has been getting heavier and more sour on an incremental basis. The need for additional hydrotreating, hydrocracking and coking has led to higher hydrogen consumption in refineries for upgrading crude oil and removing sulfur. At the same time, refiners have had to increase the acid gas removal capacity of sulfur recovery units (SRU). Furthermore, in some cases refiners have had to increase the regeneration capacity of their catalytic cracker units (FCC) in order to process heavier feedstock. Both of these capacity increases can be economically achieved by using oxygen enrichment of air.

Environmental legislation

Since 1990, the US refining industry has been impacted by increasingly strict environmental regulations. The Federal Clean Air Act Amendments (CAAA) and state requirements such as the California Air Resources Board (CARB) regulations have redefined the composition of transportation fuels, such as gasoline and diesel, to reduce air emissions from vehicles. Similarly, the European Auto Oil I introduced in January 2000 has introduced cleaner transportation fuels in the European Union. The Auto Oil II program, expected to be completed this year, will introduce even more challenging specifications for these fuels. Although these are not expected to be required before 2005, member states have introduced fiscal incentives to promote their early adoption. Gasoline and diesel fuels with sulfur contents of less than 10 ppm are already available in some countries.

The environmental regulations discussed above include more stringent limits on aromatics, olefins and sulfur content. To comply with these regulations, many refiners have had to reduce the operating severity of their catalytic reformers* to produce fewer aromatics from naphtha and increase the degree of hydrotreating of refinery products. Reducing the severity of catalytic reformers reduces by-product hydrogen supply at a refinery, while increased hydrotreating increases hydrogen demand.

The combined effect of each of these trends is that typical refineries have become significantly short on hydrogen. In the US, these factors have created supply/demand imbalances of up to 90 MMSCFD. These requirements are met by some of the largest and most sophisticated hydrogen plants ever built. They require substantial capital investment and technical know-how to achieve the high degree of plant reliability that is critical to a refinery. In the next decade, additional hydrogen demand is expected to more than double.

Buying preference of refiners

Another important driving force that is shaping the industry is a shift in the buying habits of refiners. Increasingly, refiners are choosing to buy industrial gases instead of making them themselves. Until the 1990s, a majority of the new H_2 demand was supplied by the 'make case', wherein the refiner bought a H_2 plant and operated it themselves. Air Products and Technip changed this paradigm in 1992 with a contract for the first, large, onsite hydrogen supply for a refiner in Martinez, California. Since then, a majority of the new H_2 requirements in the US have been supplied from onsite and pipeline H_2 systems owned and operated by industrial gas companies.

Crude slate shifts, stricter environmental regulations and the 'buy' versus 'make' paradigm shift are expected to be major factors in the next decade. These long term trends, which are impacting the worldwide refining industry, are expected to continue for the foreseeable future. Air Products owns and operates over 35 SMR and 17 off-gas plants with a total capacity approaching 1300 MMSCFD, making the company the global industry leader in third party supplied H_2.

Oxygen enrichment in a refinery

Oxygen is used in a refinery in the following applications: sulfur recovery, fluid catalytic cracking regenerators, spent sulfuric acid regeneration, wastewater treatment and gasification. Integration opportunities for hydrogen and oxygen production facilities and their relation to a refinery are depicted in Figure 2 and discussed below.

Sulfur recovery unit

Air Products has successfully applied O_2 enrichment to sulfur recovery units (SRU) at over 30 installations worldwide. This technology requires much lower capital investment compared to an air based plant expansion[9-11].

A refiner can expand SRU capacity depending on the level of oxygen enrichment. Figure 3 illustrates the capacity expansion for three oxygen enrichment technologies: low level enrichment, medium level enrichment and high level enrichment. A refinery's present and future sulfur balance and the need for SRU redundancy will determine technology selection.

Low level oxygen enrichment

Low level enrichment (LLE) yields ~10 - 30% SRU capacity increase with minimal plant modification and capital investment. In this approach, oxygen is injected into the combustion air main through an oxygen diffuser. The metallurgy and cleanliness of the air piping generally limits this technology to approximately 28% oxygen enrichment.

Mid level oxygen enrichment

This approach, known as the COPE™ Phase I technology, entails greater than 28% oxygen enrichment. Typically, it yields up to 50 - 60% capacity increase for a refinery rich acid gas feed (92% H_2S). Oxygen compatibility considerations at greater than 28% O_2 are critical; therefore, careful design and operation is important. Generally, a special burner with a discrete oxygen port and mixing characteristics must be employed. The refractory in the reaction furnace limits the temperature

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