Figure 1. Hydrogen is critical to convert thick, heavy, poor quality crude oil into modern day products, and to comply with strict environmental legislation.

Stephen Harrison, Linde Gases Division, Germany, and Marco Marquez, Linde North America, USA, explain how the use of hydrogen can unlock the potential of poor quality crudes processed in modern refineries.

The key to the lock

In the 21st century, the term 'scraping the bottom of the barrel' has become quite literal to the refining industry and hydrogen comes to the fore as a means to do this. Only a few decades ago, the thick, heavy crudes being utilised today would not have even been a consideration for the production of mainstream products and were used mainly as bunker fuels. 30 years ago crude quality was a good match with what was being demanded by the market, but today's refiners are being compelled to dig deeply into the dregs of the remaining resources. These crudes must be upgraded to reduce sulfur content and to keep up with market demand and environmental regulations. Hydrogen is therefore absolutely critical to convert this poor quality crude oil into modern day products, and to comply with strict environmental mandates.

Margins are tight in the highly competitive refinery business: a situation exacerbated by the costs of creating low sulfur fuels from heavier, more sour crude, as the world's crude oil resources dwindle. The sulfur content of the remaining crude is higher than ever before as oil companies are forced to tap into a cheaper but lower quality crude that requires more refining to meet tightening environmental standards while maximising margins. Product sulfur levels are lower than ever before: 30 ppm in gasoline and 15 ppm in diesel fuels.

Although these heavy crudes are actually cheaper, refineries are faced with the additional expense of upgrading to sophisticated processes to

Figure 2. Outsourcing of hydrogen supply has been widely embraced by refiners in developed countries and is being given serious consideration in many other parts of the world.

refine them to the required standards and product slate, thus meeting demand. The alternative is to pay a premium for the lighter crudes. This awkward choice has already impacted many refineries, notably on the east coast of the USA, where refineries originally built to process light and sweet crudes have had to shut down because they could not fund the technology upgrades necessary to process heavier crudes. The cost of hydrogen is part of the premium that the refiners must pay to process cheaper crudes economically.

The challenge is made more complex by the fact that no two refineries are alike and that the naturally occurring hydrocarbon distribution in crude does not always match customer demand. Various additional processing steps are required to readjust the molecules, reshape them and remove contaminants to ensure the refinery products meet the numerous requirements.

Hydrogen is a key enabler allowing refineries to comply with the latest product specifications and environmental requirements for fuel production being mandated by market and governments and helping to reduce the carbon footprint of their plants.

Growth in demand

Hydrogen is demonstrating significant growth from a global perspective. Large heavy crude oil reserves, still under development, may increase the hydrogen demand ever further. Two examples are the extra heavy crude oil in the Orinoco Belt in southern Venezuela and the Canadian oilsands. While there are many refinery configurations, all refineries harness large quantities of hydrogen across a spectrum of operations. Hydrogen is utilised in several refining processes; all aim at obtaining better product qualities. The main processes include hydrotreating of various refinery streams and hydrocracking of heavy products.

While the lighter, sweet crudes require less processing, the heavier, sour crudes contain higher levels of sulfur, other contaminants and fractions. Processing them typically begins with the same distillation process as used for the sweet crudes to produce intermediate products, but additional steps are necessary.

Hydrotreating is one such process, introduced to remove sulfur (a downstream pollutant) and other undesirable compounds, such as unsaturated hydrocarbons and nitrogen from the process stream. Hydrogen is added to the hydrocarbon stream over a bed of catalyst that contains molybdenum with nickel or cobalt at intermediate temperature and pressure (other operating conditions also factor). This process causes sulfur compounds to react with hydrogen to form hydrogen sulfide, while nitrogen compounds form ammonia. Aromatics and olefins are saturated by the hydrogen and lighter products are created. The final product of the hydrotreating process is typically the original feedstock, but free of sulfur and other contaminants. Single or multiple product streams (fractionated) are possible, depending on the process configuration.

The hydrocracking process is a much more severe operation to produce lighter molecules with higher value for diesel, aviation and petrol fuel. Heavy gas oils, heavy residues or similar boiling range heavy distillates react with hydrogen in the presence of a catalyst at high temperature and pressure. The heavy feedstocks are converted (cracked) into light distillates (for example, naphtha, kerosene and diesel) or base stocks for lubricants. The hydrocracker unit is the top hydrogen consumer in the refinery. Hydrogen is the key enabler of the hydrocracking to reduce the product boiling range appreciably by converting the majority of the feed into lower boiling products. Hydrogen also enables hydrotreating reactions in the hydrocracking process; the final fractionated products are free of sulfur and other contaminants. Other refinery processes including isomerisation, alkylation and tail gas treatment also consume small amounts of hydrogen.

A critical decision

Considering that the cost of a refinery expansion can be in the order of US$ 1 billion, with hydrogen supply representing approximately 10% of this investment in some cases, the decision concerning the optimum way to source this hydrogen has become a critical one. Refinery operators often see the investment into hydrogen supply as a defensive outlay necessary to remain competitive in the market.

Hydrogen is required in large volumes: typically 10 000 – 200 000 Nm^3/hr for a refinery. Yet it is needed for a variety of applications in several different scales of supply. Due to hydrogen representing a significant percentage of a refinery's total investment, a pivotal decision confronting operators is the supply method.

There are essentially three options for large scale hydrogen supply:

On site plant

Firstly, the refiner can build an on site hydrogen production plant, which it owns and operates using its own personnel. An advantage of this option is that hydrogen production becomes fully integrated with the other refinery processes. While this enables the refinery to keep control of its own hydrogen supply, this option requires more capital and demands skilled attention from the refinery labour force for efficient operation, maintenance and repair. If the in house team is unable to operate the plant efficiently, the refinery will incur financial losses, including increased consumption of natural gas and even other more costly raw materials such as naphtha, water and power. Loss of hydrotreated products attributed to poor reliability may also be a concern.

Outsourcing

The second option is to outsource hydrogen supply to an experienced industrial gas service provider. Compared to on site hydrogen production, the advantages here are that no capital investment is required

Figure 3. The cost of hydrogen is part of the premium that the refiners must pay to process cheaper crudes economically.

and the risks in terms of operation, maintenance, capital overrun, raw material overconsumption, schedule and labour issues are all transferred to the service provider in exchange for a monthly service charge. The potential disadvantage, from the refiner's perspective, is the reliance on a third party to supply a critical reactant for their processes. However, this 'over the fence' concept has been widely embraced by refiners in developed countries, and is given serious consideration in many other parts of the world.

On site recovery

Thirdly, the refiner could recover the hydrogen needed from existing hydrocarbon streams. Lower purity hydrogen can be recovered and purified from catalytic reforming, purge stream or other refinery sources such as refinery off gas, via methods such as pressure swing adsorption and cryogenic systems. This option is limited by the availability and quality of hydrogen containing streams in the refinery. However, it may supplement the first two options.

Small scale use

Hydrogen can also be used on a smaller scale in the refinery (less than 1000 Nm^3/hr). In these cases hydrogen can be brought in and stored on site in a liquefied form and further vaporised to be used as gaseous hydrogen. Other forms of supply include a hydrogen tube trailer delivered by a third party supplier hooked to the back of a truck or 'bundle' delivery, which involves a bundle of 12 – 15 cylinders delivered to the refinery site. Bundle supply is typically used to support hydrogen needs during start up and possibly in an on site pilot plant where research and development work is being conducted, such as experimental hydrogenation studies. Individual cylinders also have their place in refineries to keep on site laboratories supplied with hydrogen. Some of these laboratories also make use of bench top generators that produce hydrogen by electrolysis of distilled water.

Process control and leak detection

In addition to its mainstream uses, hydrogen is utilised further in refineries for smaller but no less critical applications. Monitoring and measurement of refinery processes demands accurately calibrated instrumentation using mixtures containing high quality certified specialty gases. The typical instrumentation required for monitoring refinery operations includes a gas chromatography flame ionisation detector (GC-FID).

These analytical instruments use zero gases, span gases and calibration gases to control chemical processes. Fuel gases (such as hydrogen) are needed if flames are part of the system, as they are in GC-FID, and gas chromatography (GC) requires a carrier gas, which will often be hydrogen. All of these gases must be of an exceptionally high and controlled quality in order to obtain the very accurate analytical results required in modern refineries.

Hydrogen is one of the smallest and lightest molecules, but is also one of the most flammable and explosive gases processed at a refinery. Any leakages pose a possible risk of fire or explosion, potentially resulting in damage to capital

Figure 4. When smaller quantities of hydrogen are required, it can be supplied by tube trailer, stored on site in liquefied format and then vaporised for use as gaseous hydrogen.

equipment, production downtime and, at the extreme end, potential loss of life. Since hydrogen is used on such a refinery wide scale, it is critical to detect any leaks and, as such, there is a vital need for sophisticated detection equipment.

Gas detectors are used to monitor and warn of the existence of specific toxic or combustible gases and oxygen deficiency hazards. Typical measurement levels will be in the low parts per million for toxic gas, while combustible gases are measured in percent lower explosive limit (LEL). Oxygen deficiency is measured at the percentage level.

Gas detection monitoring devices can be classified in one of three ways. A fixed system refers to a monitoring system permanently installed in the workplace. The detecting sensor may be hard wired or use wireless signals transmitting to a central reporting station. Most will come with an audible alarm. Fixed gas detection can be used indoors, as well as having outdoor use as a perimeter monitor with chemical manufacturing and petrochemical sites.

Portable gas detection refers to gas detectors that are worn or carried by an individual. Typically battery operated, portable monitors are used for toxic or combustible gas detection, as well as for oxygen deficiency monitoring in confined spaces. Linde Gas recently launched its G-TECTA™ portable gas detection instruments designed for simple application with maximum protection against hazardous working conditions. These multi gas detectors are worn on the clothing of plant personnel and can be configured to detect up to 26 different gases. The detectors are equipped with alarm systems and a vibration action so the user is also given audible and physical warnings of a potentially explosive environment, noxious gases or oxygen displacement.

Area monitoring detection offers the benefits of a multi gas fixed system in a transportable unit. These units are designed for team protection or area surveillance for short term work where fixed gas systems are not suitable.

All refinery gas detection equipment also needs to be tested and calibrated regularly and accurately. Linde Gas has addressed this requirement by developing its ECOCYL® range: small, environmentally friendly and portable refillable gas cylinders with completely integrated valve, pressure regulator and flow meter for direct use.

Environmentally friendly

In today's highly advanced refining industry, it is becoming increasingly common to find synergies between hydrogen and other processes, such as the recovery or sequestration of carbon dioxide, wastewater treatment and enhanced oil recovery (EOR). The hydrogen production process can be harnessed to sequester carbon dioxide, which is a byproduct of this process. Instead of venting carbon dioxide into the atmosphere, the plant design can add additional steps to the hydrogen process to remove carbon dioxide from the gaseous stream and recover it for other industrial uses. An interesting and pertinent application for this carbon dioxide is EOR, where carbon dioxide is pumped at high pressure into deep oil wells to improve the recovery of the petroleum crude oil trapped at these low levels.

Hydrogen is also used to enable the production of biofuels, produced from biological matter instead of fossil fuels. This matter can range from corn or soybeans to crop oils and animal fat, depending on the type of fuel being made and the production method. Generally speaking, biodiesel is an alternative source of fuel to standard diesel fuel that is made from biological ingredients instead of crude oil. Biodiesel is non-toxic, renewable and also sustainable, because it essentially comes from plants and animals, which can be replenished through farming and recycling.

The newer generation of biodiesel can be used in diesel engines with little or no modifications. Although biodiesel can be used in its pure form, it is usually blended with standard diesel fuel. Hydrogen is needed in certain biofuel production processes, including hydroprocessing or the catalytic upgrading of oil products. Scandinavia, the USA, Argentina and Asia are leading developments in this field.

Technology in action

One of the core business focus areas of Linde is as a single provider of all hydrogen supply options for oil refineries, ranging from engineering an entire hydrogen supply solution, including operation and maintenance, to assisting with hydrogen recovery from existing networks.

In depth hydrogen supply studies help to identify customers' potential optimisation opportunities through improving processes, reducing power consumption and limiting future hydrogen demand. Typical hydrogen study objectives are geared towards optimising the refinery hydrogen balance by using a comprehensive evaluation of the entire hydrogen network. An accurate assessment of the existing hydrogen network is essential to understand it and enable further optimisation. Deliverables include an assessment of the customer's existing hydrogen balance, recommendations to optimise it and recommendations on how to design for future needs, including economical and technical benefits that can be obtained from each scenario.

One recent success story involved a study to evaluate a refinery's overall hydrogen network system. The refinery, a large reformer hydrocracker plant with several hydrotreating units, was planning several profit improvement initiatives that included clean fuel and biofuel production, as well as processing of opportunistic heavy crude. It was anticipated that these initiatives would increase future hydrogen needs by more than 30%. To meet this forecast, the refiner sponsored a study to determine the available hydrogen recoverable from its existing system and the best solution to meet future incremental demand.

At the time of the study, hydrogen was being sourced from the catalytic reformer, an old steam methane reformation (SMR) and a hydrogen recovery unit (HRU). In addition to many off gas streams from the usual process units, several off gases from a nearby chemical plant were also available as potential sources of hydrogen. Various hydrogen producer and consumer sources needed to be carefully analysed in order to optimise the hydrogen network, therefore providing the best future solution.

Upon completion of the study, several options including recovery, debottlenecking the existing SMR, and new SMR were presented to the refinery (Table 1). It was concluded that a modern HRU would provide the lowest cost hydrogen for the refinery to meet future needs, while also emitting the lowest level of greenhouse gases. However, as this option depended strongly on availability of off gases from the nearby chemical plant, further in house risk assessment was needed. The next low cost option was a new and larger SMR as an alternative and reliable solution, although requiring higher capital investment, to meet the hydrogen requirement. To assist the refinery in minimising capital investment, a build/own/operate scheme was offered by Linde. The refinery client agreed with the study conclusion that off gas recovery is most cost effective option to meet the pending hydrogen need.

Table 1. Comparison of options to recover and produce hydrogen [1]

	Existing operation	Rerate SMR	Modified SMR	New SMR	Recovery option	Heavy oil gasification
Hydrogen production (tpd)	Base	+100%	110%	163%	208%	163%
H_2 purity (% H_2)	Base	+5%				
CO_2 emission (tpd)	Base	190%	110%	128%	0%	192%
Average H_2 cost (cost/ H_2)	Base	101%	104%	92%	85%	164%
Meet future demand	No	Yes	No	Yes	Yes	Yes

[1] *All cases compare against base case*