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Strategic links:

# The role of oxygen and hydrogen in refining.

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The commoditised refining industry finds itself subject to ever increasing competitive pressures. In mature markets small and mid-sized refineries have to compete with large, integrated complexes recently built in emerging markets which enjoy the benefits of easier access to feedstock and lower labour costs, 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 world's diminishing crude oil resources is higher than ever before as oil companies are forced to tap into a cheaper but lower quality of crude that requires more refining to meet tightening environmental standards and while maximising margins. To be competitive in this challenging landscape, modern refineries must operate efficiently, ensure adequate capacity, and control emission levels. Operators are therefore keen to maximise profitability factors, often by optimising the efficiency of their assets. State-of-the-art technologies can help unlock opportunities in such a volatile market. However, with investment budgets limited, new technologies must offer a high return on investment coupled with a short payback period.

At the same time, refineries face growing environmental pressures. Environmental regulations – NOx regulations in particular – are getting stricter and this trend is expected to continue. Worldwide, California has typically been the regulatory trendsetter, raising the bar for strict environmental emission limits in America and beyond. This is particularly true of the state's South Coast Air Quality Management District (SCAQMD).

Effective from 1 January 2015, the SCAQMD's Rule 1146 limits NOx releases from industrial and commercial boilers, steam generators and process heaters to less than 9 parts per million (ppm). By 2016, the threshold for NOx emissions will fall to 5 ppm or lower. Looking ahead, other geographies are bound to follow suit with tighter NOx controls that are more in line with the Californian example.

A refinery has anything between a few to over a hundred furnaces. With the complexity of so many emission sources, and tightening regulations, refiners have the challenge of optimising net emissions across their entirety of their site or from individual sources. From an economic point of view, it is generally not feasible to install post-combustion techniques, such as selective catalytic reduction (SCR), on all NOx emitting sources. Neither is combining flue gas streams – nor would it be conducive to maintenance. As such, operators have tended to focus on the main originating sources of emissions such as fluid catalytic crackers. However, as regulations become more stringent, additional combustion operations in the refinery need to contribute towards NOx reduction.

The refinement of oil into fuels, chemicals and a variety of polymers for plastics production is a complex, energy-intensive process. Refining steps like distillation, catalytic reforming, thermal cracking, hydrodesulfurisation and hydrocracking require a lot of heat. To generate this heat at the required temperatures, hydrocarbon fuels are burned in fired heaters. Positioned at the heart of a refinery, fired heaters play a central role in overall profitability. Not only are these heaters the main source of emissions, they are also the main consumers of energy. Hence operators are challenged to ensure that their fired heaters are working optimally and, most importantly, are not limiting overall refinery performance. Fired heaters, particularly after a unit revamp, can often become bottlenecks in the production chain.



## Oxygen enrichment (O<sub>2</sub>e) in process furnaces

Operators typically consider upgrading their plants to overcome furnace bottlenecks. This move is mainly prompted by a need to increase efficiency or meet stricter environmental regulations. This solution, however, is both costly and time-consuming, and high CAPEX investments of this nature are difficult to enact in times of economic instability or high risk. Operators may even need to replace their entire furnace to capitalise on a capacity-driven opportunity, but this could entail a lengthy implementation cycle and be subject to space restrictions. In some cases, stricter environmental legislation may require operators to install new, lower-emissions burners with larger flame volumes, which impinge on the tubes in the coil. This can affect both the radiant and convection sections.

Given the cost, risk and potentially long downtime associated with upgrades or new facilities, many operators welcome a more flexible, lower CAPEX solution.

One such way of optimising a heater's performance is by adjusting the process parameters of the fuel mix or the excess air. One approach for debottlenecking process fired heaters is based on oxygen enrichment, which focuses on combustion air as a key operating parameter that can be adjusted to optimise furnace performance. With this system, operators can vary the oxygen content in the combustion air to enhance furnace efficiency. Oxygen enrichment is a low CAPEX reversible solution and is an ideal strategy for operators looking for a low-risk, high-return and short payback route to enhanced furnace operations.

Oxygen enrichment is a widely established technology in refining and is successfully used for sulfur processing in Claus units and in the regeneration section of fluid catalytic cracking units (FCCU) and low-level oxygen enrichment solution can be tailored specifically to the needs of fired heaters. By modifying the burner design, this technology increases the efficiency, capacity and lifecycle of furnaces.

Oxygen enrichment can provide refinery operators with maximum flexibility as it can be implemented in different ways. One option involves modifying the existing burner. For example, Linde can convert an existing fired heater burner into a LowNOx burner, an enhanced oxygen lancing technology. This modification approach offers the lowest CAPEX. Alternatively, a new LowNOx burner can be deployed. The oxygen installation and control system are integrated into the existing control system (DCS/PLC) for ease of management and smooth safety interlocks. Regardless of the deployment option, oxygen enrichment can be implemented without modifying the furnace structure. It can also be adapted to any kind of configuration (balanced, induced, forced and natural draft) so operators still have the option of running their furnace in air mode.



O<sub>2</sub>e is a low CAPEX reversible solutions ideal for operators looking for low-risk, high-return route to enhance furnace operations.





## Oxygen enrichment for de-sulfurisation

Almost every oil field produces crude with a unique mixture of characteristics, which presents distinct challenges to refiners involved in separating crude into different products. In addition to sulfur content, refineries are being challenged to manage increased levels of acid gas or sour water stripper gas and the occasional lean acid gas feed.

For refiners, throughput can be limited by the speed at which plants can de-sulfurise crude. However, the more stringent the de-sulfurisation process becomes, increasing Claus plant loadings with hydrogen sulfide and ammonia, the more frequently bottlenecks in the production process also become. Claus plants operating in refineries process concentrated hydrogen sulfide fractions, converting them into elemental sulfur. The technology is also able to destroy contaminants, particularly ammonia.

Oxygen enrichment of the combustion air significantly increases sulfur handling capacity. Associated benefits include increased productivity achieved without changing the pressure drop, more effective treatment of ammonia-containing feeds and less effort required for tail gas purification (reduced nitrogen flow). Oxygen enrichment is also a highly customisable approach to improving Claus plant yield with options varying from low level oxygen enrichment to employing advanced proprietary technology to bring about capacity increases of up to around 150 percent.

In practical terms, this means that refineries can delay new Claus investment decisions as they can extend their existing Claus plant capacity. This is a particular advantage to those refineries whose plant footprints cannot accommodate the introduction of additional Claus plants.

However, when even greater capacity is needed and increased levels of oxygen beyond 28 percent are required, it is necessary to introduce the oxygen into the reaction furnace separately from the air supply, as the combustion-air piping in conventional sulfur plants and air-only burners are unsuitable for use with highly enriched air.

SURE® burners from Linde Gas are addressing this challenge. They are self-cooled tip-mix burners with separate ports for acid gas, oxygen and air supply. The burners can be used in both end-fired and tangential-fired furnace designs and can achieve excellent mixing of hydrogen sulfide and oxygen enriched air over a wide load range.

The intensive mixing characteristics of these innovative burners have been developed through extensive test work at Linde's own pilot plant – a commercial scale sulfur recovery unit – harnessing computational fluid dynamics (CFD) modelling to achieve excellent contaminant destruction and significantly increased tonnage output.





For operation with high levels of oxygen enrichment – greater than 45 percent – methods must be employed to mitigate high flame temperature in the reaction furnace. The SURE double combustion process is the best available technology, providing full capability at up to 100 percent oxygen in an uncomplicated process that is easy to install, operate, and maintain.

Double combustion, as the name implies, splits the heat release into two separate reaction furnaces with cooling between. In the first reaction furnace, all amine gas, sour water stripper gas and, if required, air, are fed to the SURE burner together with the supplied oxygen, the level of which depends on plant throughput. The tip-mix burner allows for thorough mixing, giving excellent contaminant destruction efficiencies.

There is no sulfur condenser between the first waste heat boiler (WHB) and the second reaction furnace. Also, there is no burner in the second reaction furnace. By design, the gases exiting the first WHB and entering the second reaction furnace are substantially above the auto-ignition temperature of hydrogen sulfide and sulfur vapour, under all normal and turn-down operation conditions. This system allows for low-pressure drop, which is easy to control and easy to install.

The result of this type of control is a temperature profile ideally suited to the Claus process. Operating temperatures in the first reaction furnace are high enough to destroy ammonia and hydrocarbons, but remain well below refractory limitations.

A novel approach has used the benefits of a multi-pass WHB for plants with restricted footprint. The zone between the first and second passes of the boiler is utilised as the second reaction furnace of the double combustion process. In this situation, lances are installed in the channel head connecting the first and second pass of the WHB tube sheets (where the remaining oxygen can be added). For the optimum design and location of the SURE burner and oxygen lances, Linde uses a validated CFD model.

The change-out of the WHB can improve energy efficiency at a plant through the generation of valuable high-pressure steam. Other energy efficiency benefits arise from the much-reduced process gas flow through the plant. This reduces the converter reheat and incinerator fuel gas requirements to a minimum – and reduced energy requirements mean significantly reduced carbon dioxide emissions.

**SURE** double combustion provides full capability at **up to 100% oxygen** and is easy to install, operate and maintain.

## Bridging the oxygen enrichment gap

SURE burners or other oxyfuel burners in Claus units are designed for air-only operation for mid-level or high-level oxygen enrichment. These applications usually start at enrichment levels of 28 percent by volume of oxygen in the enriched process air. But sometimes oxygen levels below 28 percent can be sufficient to adequately cover capacity increases, realise energy savings and accelerate kinetically limited reactions like destruction of ammonia ( $\text{NH}_3$ ). In these instances, low level oxygen enrichment technology such as Linde's OXYMIX® Injector and OXYMIX Flowtrain metering system can be combined with SURE burners to deliver the desired results and provide refinery customers with high flexibility in capacity.

The additional oxygen and the air have to be mixed completely within a short mixing distance to obtain smooth oxidation in the reactor and a reliable oxygen analysis. The OXYMIX Injector's design, based on computational fluid dynamics simulations, forces the oxygen into the air flow at a specific angle through a circle of nozzles, providing a thorough mixing within a short mixing distance. The OXYMIX Flowtrain meters oxygen into the process air until the desired concentration is reached. High oxygen concentrations near the pipeline wall are prevented and operational risks of oxygen enrichment are reduced.

Benefits include up to 30 percent in capacity increase, 45 percent reduction in NOx emissions, up to 5 percent increase in efficiency levels, additional firing capacity due to the lower flue gas volume and a wider window of operating conditions.

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## Hydrogen for hydrotreating

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. Thirty 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 and must upgrade these crudes 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.

Although these heavy crudes are actually cheaper, refineries are faced with the additional expense of upgrading to sophisticated processes to refine them to the required standards and product state 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 United States, where refineries originally built to process light and sweet crudes have had to shut down because they could not fund the technology upgrade 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 re-adjust the molecules, reshape them and remove contaminants to ensure the refinery products meets the requirements for end-use and the product demand profile, as well as environmental performance.

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.

From a global perspective hydrogen is demonstrating significant growth. 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 of Venezuela and the Canadian Oil Sands. 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 aiming 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 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, pressure and other operating conditions. 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 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 to 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.

**H<sub>2</sub> is critical to convert poor quality crude into modern-day products.**

# Getting ahead through innovation.

With its innovative concepts, Linde is playing a pioneering role in the global market. As a technology leader, it is our task to constantly raise the bar. Traditionally driven by entrepreneurship, we are working steadily on new high-quality products and innovative processes.

Linde offers more. We create added value, clearly discernible competitive advantages, and greater profitability. Each concept is tailored specifically to meet our customers' requirements – offering standardised as well as customised solutions. This applies to all industries and all companies regardless of their size.

If you want to keep pace with tomorrow's competition, you need a partner by your side for whom top quality, process optimisation, and enhanced productivity are part of daily business. However, we define partnership not merely as being there for you but being with you. After all, joint activities form the core of commercial success.

**Linde – ideas become solutions.**



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