Safe operations, environmental compliance and product quality for refinery heavy residue gasification

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Petcoke gasification

The chemistry of gasification fits somewhere between combustion and pyrolysis. Combustion is a high temperature reaction in an excess of oxygen. It produces heat, carbon dioxide and steam. Pyrolysis is the high temperature decomposition of a hydrocarbon to form solid carbon in the absence of oxygen. It is used to produce coke from coal in steel making.

Gasification is a high temperature process which needs a precisely controlled concentration of oxygen which is often supplied from an air separation unit (ASU). Gasification is increasingly being used on refineries to process petcoke, a heavy residue from coking units.

Today, one of the world's largest gasification projects is at the Jazan refinery in Saudi Arabia where more than a dozen gasifiers built by Técnicas Reunidas will produce syngas from petcoke.

One of the drivers behind refinery residue gasification projects has been the IMO 2020 regulation which has increased the demand for low sulphur marine fuels. Furthermore, petcoke has recently been banned in India for use as cheap feed to coal fired power plants due to its high sulphur content. Instead, gasifying it to produce syngas and hydrogen, which is used to desulphurise or hydrogenate fuels, can create value from the petcoke.

Gasification projects require some of the world's largest ASUs

At Jazan, the gasifiers will produce enough syngas to generate 4 GW of power and steam. The syngas is fired directly in gas turbines which produce 2,400 MW of electricity in an integrated gasification combined cycle (IGCC) power

Coke ovens on a Steelmaking plant in Turkey

Coker unit on a refinery

Petcoke – a heavy residue from crude oil refining

Image courtesy of Air Products and Chemicals Inc. Four gasification reactors at Lu'an, China

Image courtesy of Air Products and Chemicals Inc. Four ASUs to feed the gasifiers at Lu'an

plant. The syngas-island will also export hydrogen and steam to the refinery. The gasification process consumes vast quantities of oxygen. In order to feed the gasifiers at Jazan, the process requires six mega ASUs, each one rated at 3000 Tonnes per day of oxygen. Air Products has been instrumental in the Jazan refinery heavy residue gasification project and has secured a strong gasification technology position through the acquisition of GE's Gasification business and Shell's coal gasification technology.

Coal and petcoke have similar properties as gasification feedstocks. Both can be used to yield hydrogen for the refinery or chemicals production. The Lu'an coal to chemicals project at Changzhi in China's Shanxi province, is large coal gasification project. Four gasification reactors have been constructed to supply syngas to a chemical complex and four large Air Products ASUs feed the gasifiers with oxygen. A methanol-based syngas clean up plant sits downstream of the gasifiers.

Switching from China to India, the ten gasification reactors at the Reliance refineries at Jamnagar are designed to run on petcoke and for flexibility can also operate on a mixture of 35% coal and 65% petcoke. They are fed by five of the world's largest ASUs, each rated at 5,250 Tonnes per day of oxygen. The target products from the project include hydrogen for clean fuels processing and syngas.

In the past, coal gasification and steel blast furnaces were the two largest consumers of oxygen from ASUs. The tide is turning, and refineries are now joining the super-league of oxygen consumers with catalyst regeneration and gasification applications driving oxygen demand.

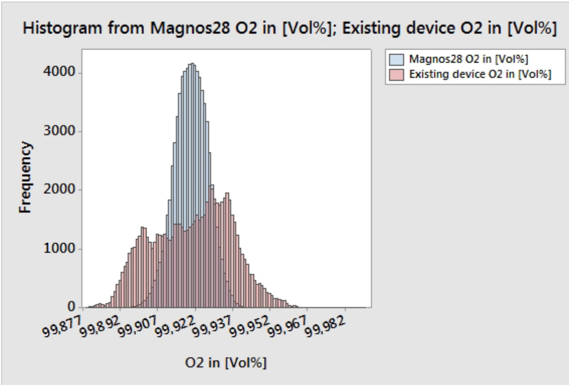
Gas quality - oxygen purity matters

"The ASUs at Jamnagar are incredible" says Bodhistaya Das, an ex-Linde ASU Process Design and Commissioning Engineer who has operational experience at the Reliance Jamnagar ASU complex. He is now a Process Control Engineer working in India. "The diameter of the High-Pressure distillation column trays is huge at 7m. To work at this scale, we had to overcome some technical challenges in designing the six-stage cascade reboiler-condenser unit between the low-pressure and high-pressure distillation columns. In addition to process effectiveness, safety is a major concern for this piece of equipment because hydrocarbon accumulation in the liquid oxygen sump must be avoided".

The oxygen produced on the Reliance ASUs is at 99.5% purity and the argon from the process is used to improve the overall energy efficiency. This contrasts to a standard ASU design which is optimised to produce oxygen at between 99.6 and 99.8% purity and export argon as a liquid product. This higher oxygen purity means that most of the argon from the air can be captured for sale as a valuable co-product.

Jamnagar, India

ABB Magnos28 paramagnetic oxygen gas analyser



Magons28 achieves improved oxygen measurement accuracy and repeatability

Commenting on the implications of argon recovery from air separation, Stephen Gibbons, Head of Product Management for the continuous gas analyser product range within ABB's Measurement & Analytics business line says that "paramagnetic oxygen gas analysers have been used for decades by ASU operators to measure the amount of oxygen in the feed to the argon column and to analyse the final oxygen purity. It is the final oxygen purity where repeatable and accurate oxygen gas analysis is essential to minimise argon losses and maximise profits".

The monetary value of an inaccurate oxygen reading at 99.7% when the reality is an oxygen purity at 99.6% means that 0.1% of the oxygen flow is high value argon which is being sold at the lower price of oxygen. That's a discount that few ASU operators can afford. Gibbons adds that "the new Magnos28 incorporates our innovative microwing. This is a digitalised, solid-state version of the gas-filled dumbbell that has been used in paramagnetic gas analysers for decades. It results in less drift on the measurement and better accuracy, which means that ASU operators can know exactly where their argon is going. Upgrading to the new Magnos28 enables ASU operators to minimise argon losses and maximise their profits".

Oxygen sump hydrocarbon analysis and process safety

In 1997 ASUs at the Fushun Ethylene complex in China and the Shell Gas to Liquids plant at Bintulu on the island of Sarawak suffered catastrophic explosions. In each case the root cause was traced back to abnormally high levels of contamination in the ambient air: soot particles from forest fires in one case and ethylene in the other. Also, in both cases, the combination of liquid oxygen, combustible hydrocarbon material and aluminium used to construct the ASU reboiler led to a massive explosion and fire. Lessons from

Bintulu on the Island of Sarawak, Malaysia

the Bintulu and Fushun ASU reboiler explosions have been captured in the EIGA doc 65/13: 'Safe operation of reboilers/condensers in air separation units'. These lessons are of direct relevance to ASUs located close to refinery sites.

"In ASU design and operation, safety is the number 1 priority" says Bodhistaya Das, an Ex-Linde ASU expert. "The main precautions against hydrocarbon contaminant build up in the ASU focus on CO_2 measurement at the outlet of the pre-purification unit (PPU), which is located at the warm end of the ASU, and hydrocarbons analysis in the cryogenic liquid oxygen sump. Detection of CO_2 breakthrough from the PPU is a warning that hydrocarbons such as methane or ethane are not being removed by the PPU and might therefore be entering the ASU".

ABB LGR-ICOS gas analyser for on-line acetylene measurement

Analysis of hydrocarbons in the cryogenic liquid where there is the highest potential concentration of hydrocarbon contaminants, generally by extraction of liquid oxygen from the main reboiler sump, is the second line of defence. This can be achieved using a total hydrocarbon (THC) gas analyser.

Das develops the point further: "for an ASU with pumped liquid oxygen withdrawal, such as the ones I operated at Jamnagar, the accepted threshold is 500 VPM methane equivalent of total hydrocarbons in the liquid oxygen. Continuous removal of the liquid oxygen significantly reduces the risk of hydrocarbon build up, but this doesn't diminish the importance of a properly designed front end section. At places like refineries where the hydrocarbon content in the ambient air is higher than usual, an additional specialised layer of adsorbent is added to the PPU to remove butane and higher derivatives. Analysing the typical ambient air composition before designing an ASU is also of paramount importance".

Stephen Gibbons comments that ABB has a range of established and innovative solutions for hydrocarbon analysis for safety on ASUs. "Our Fidas24 gas analyser has been used on many ASUs for decades and is trusted by operators and plant-builders worldwide. For THC measurement it is a tried and tested option".

According to the EIGA doc 65/13, ASUs that use a reversing heat exchanger must also conduct routine analysis of acetylene in the liquid oxygen from the main reboiler sump. Gibbons confirms that "most operators are looking to detect acetylene at less than 0.5 VPM. Reliable and precise continuous techniques for acetylene measurement in the sub-VPM level are not common but we believe that our LGR-ICOS analyser is up to the task. This innovative laser technique is capable of accurate trace hydrocarbon measurements in a complex background gas matrix".

As a bonus, the LGR-ICOS requires no consumable gases and has minimal calibration gas mixture requirements. This simplifies gas analyser maintenance and reduces the cost of ownership. It adds up to safe and profitable ASU, gasification and refinery operations.

Syngas islands and environmental compliance

Jazan, Jamnagar, Lu'an and other major gasification projects are giving birth to new terminol-

Refinery and gasification emissions to air require CEMS

Advance Optima 2040 gas analyser configured with two NDIR channels for simultaneous CO and CO_2 measurement

ogy: ‘syngas island’. Whilst the refinery may target hydrogen from the gasification process as the core reason for the investment, the gas flowing from the gasifiers is a crude mixture of carbon monoxide, hydrogen and other acid gases such as carbon dioxide and hydrogen sulphide. After the gasifier come the acid gas removal and hydrogen purification processes. The gasifier, ASU, syngas clean-up and hydrogen purification process cluster is referred to as a ‘syngas island’. It is often the case that the residual carbon monoxide will be burned to generate heat or power. Or, increasingly, it is used for petrochemicals production, as refiners seek to diversify their product mix beyond fuels.

With a feedstock of petcoke or coal, the emissions from the gasifier will inevitably contain a range of acid gases. Hydrogen chloride, hydrogen fluoride and hydrogen sulphide to name a few. Ammonia is also likely to be present. These should be removed from the process by the acid gas removal system. To validate that everything is under control, an FTIR gas analyser is ideal. A single FTIR instrument can measure as many as 15 chemicals at one time, including these highly reactive gases. Coming back to ABB’s Steve Gibbons, he says that “the ACF5000 is the global benchmark FTIR for CEMS applications”. With more than 2000 units installed around the world, ABB has some substance to back up their claim. “In emissions monitoring applications, these analysers ideally need to operate with 100% accuracy 100% of the time” says Gibbons. “That’s where the ACF5000 leads the pack. In recent certification testing, we were able to prove the reliability of the gas analyser and extend its maintenance interval from 6 to 12 months. That underlines the reliability of our equipment and means lower maintenance costs for the operator”.

Refinery hydrogen purification and quality control

After the syngas clean up process, the next step is hydrogen purification. This is achieved on a pressure swing adsorption (PSA) unit. To measure hydrogen concentrations, the classical instrument would be a thermal conductivity (TCD) analyser. However, most operators choose a non-dispersive infrared (NDIR) gas analyser to measure the final hydrogen gas purity.

Hydrogen is not IR-active, so why is the NDIR the default option? “NDIR analysers are ideal for measurement of the final hydrogen purity”, says ABB’s Gibbons. “It’s generally taken for granted that the gas coming off the PSA will be hydrogen but what really matters is the absence of carbon monoxide (CO) and carbon dioxide (CO2). These two gases are poisons to the hydro-treating catalysts in the subsequent processes where the hydrogen is used in the refinery. The hydrogen product specification will generally have a maximum total combined CO and CO_2 content of 10 parts per million by volume. Simultaneous measurement of these two components is exactly what our NDIR gas analyser, the Uras26, does best”.

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