Refinery hydrogen from petcoke gasification

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As old as the hills

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.

Coking is as old as the hills. The town of Redstone in Colorado is now a well-known tourist attraction. In 1900 about 250 ovens were converting 6 million tpy of locally mined coal to coke for use in nearby metallurgical industries.

Coke ovens in Redstone, Colorado.

At a similar time, the Seattle Gas Light Company coal gasification plant in the State of Washington was producing 7000 Nm^3 per hour of town gas which was used for heating and lighting in nearby suburbs. Town gas is a flammable mixture of hydrogen and carbon monoxide generated by the gasification process. On the refinery and petrochemicals complex, it is known as syngas today.

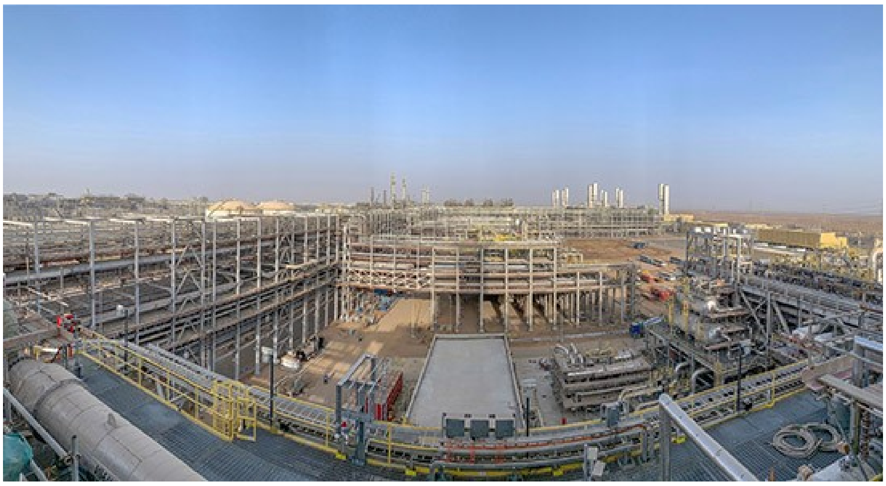
Gasification is undergoing a renaissance. It is a high temperature process which needs a precisely controlled concentration of oxygen which is often supplied from an air separation unit (ASU). Gasification is increasingly being used on refineries to process petcoke, a heavy residue from coking units. The process uses oxygen to make hydrogen, the lightest of all gases, from petcoke – the heaviest of all refinery residues.

Fast-forward to mega-scale refinery petcoke gasification projects for the 2020s

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 the Spanish Company Técnicas Reunidas will produce syngas from petcoke, a heavy refinery residue.

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 sulfur content. Instead, gasifying it to produce syngas and hydrogen, which is used to desulfurise or hydrogenate fuels, can create value from the petcoke.

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 2400 MW of electricity in an integrated gasification combined cycle (IGCC) power plant. The syngas-island will also export hydrogen and steam to the refinery. The gasification process consumes vast quantities of oxygen. To feed the gasifiers at Jazan, the process requires six ASUs, each one rated at a phenomenal 3000 tpd 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.



Jazan refinery and integrated gasification combined cycle power plant under construction.

Refinery hydrogen purification and quality control

After petcoke gasification, the next steps are syngas clean-up and hydrogen purification. Hydrogen is separated from CO and CO2 using a pressure swing adsorption (PSA) unit. To analyse hydrogen concentrations, the classical instrument of choice is a thermal conductivity (TCD) gas analyser. However, most refinery hydrogen plant 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 Stephen Gibbons, Head of Product Management for the continuous gas analyser product range within ABB's Measurement & Analytics business line. "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 hydrotreating 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 CO2 content of 10 ppm by volume. Simultaneous measurement of these two components is exactly what our NDIR gas analyser, the Uras26, does best".

Gasification consumes vast quantities of oxygen to make

hydrogen

Coal and petcoke have similar properties as gasification feedstocks. Both can be used to yield hydrogen for the refinery or for chemicals production. The Lu'an coal to chemicals project at Changzhi in China's Shanxi province is a large coal gasification project. Four gasification reactors have been constructed to supply syngas to a chemical complex and four large ASUs feed the gasifiers with oxygen. A methanol-based syngas purification 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 a staggering 5250 tpd of oxygen. The target products include hydrogen for clean fuels and syngas.

Refineries are becoming major oxygen consumers with applications ranging from cat-cracker catalyst regeneration to gasification driving demand growth. To produce oxygen at the scale required by modern refinery operations, on-site production using mega-scale ASUs is required.

Petcoke storage.

On the ASU, oxygen purity matters

"The ASUs feeding the gasifiers at Jamnagar are incredible" injects 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 7 m – that's huge. 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.

Commenting on the implications of argon recovery from air separation, ABB's Gibbons 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 maximise their profits".

Oxygen 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 incident 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. In both incidents, 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 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 CO2 measurement at 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 CO2 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".

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".

For the THC measurement, many instrument engineers will be familiar with the flame-ionisation-detector (FID) type of gas analyser. This technology has an established history in this application and can be operated either with, or without a methane cutter to provide THC and non-methane HC (NMHC) readings. Whilst the technique is robust, it does require specialty gases grades of high purity hydrogen and instrument air for its operation to create the flame. Cylinder change overs of these consumable gases are required in addition to occasional calibration using a certified specialty gas mixture. Gibbons says that ABB has a range of established and innovative solutions in this area: "Our Fidas24 gas analyser has been a default choice for years. However, for convenience and additional speciation within the hydrocarbons we believe that our Uras26 NDIR instrument is worth consideration. It can be configured to measure up to four separate IR-active species, for example: methane, ethane, ethylene and propane". These are some of the main hydrocarbon contaminants that have the potential to accumulate in the liquid oxygen in the ASU main reboiler sump.

ABB supplies gas-filled cells in the Uras26 NDIR analyser so that it can frequently run an automatic test and calibration sequence. This provides the confidence that the instrument will respond accurately and eliminates the costs of consumable calibration gas mixtures and minimises intervention from the maintenance team.

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.

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Read the article online at: https://www.hydrocarbonengineering.com/special-reports/11062020/refinery-hydrogen-from-petcoke-gasification--the-lightest-of-gases-from-the-heaviest-of-residues/