Managing enterprise risk

Cryogenic safety in air separation units

By Stephen B. Harrison

Safety beats in the heart of industrial gases. There are inherent hazards in our operations and a primary role of management is to minimise the risk that these hazards would escalate to become accidents. Some risks have the potential to blow the whole company off course – these are referred to as 'enterprise risk' and they deservedly get plenty of attention in the boardroom.

Process safety can be done in a very scientific way, using computer modelling and analytical tools to quantify the infinitesimal probability of a catastrophic failure. Looking at a probability of one chance in several billion on a spreadsheet can perhaps leave us feeling that the risks are hypothetical. Looking at the images of the devastated ASU site at the Henan Gas Group Yima gasification plant in Sanmenxia in China, reminds us that the hypothetical situation can, and does, occasionally become the tragic reality. Fifteen people lost their lives as a result of that explosion in July 2019, and 16 others were seriously injured.

What went wrong at Yima?

The preliminary accident investigation following the ASU explosion at the Yima[1] gasification plant says that, "the direct cause of the accident was that the leakage of the cold box of the air separation device was not handled in time and 'sand explosion' occurred."

As the cryogenic liquid vaporised, it scattered the perlite insulating material from the cold box, which then collapsed onto a $500m^3$ liquid oxygen storage tank. Further explosions and fires followed.

The grounds for asserting that the leak was not dealt with quickly enough are clear. The report attests that on 26th June, it was noticed that the oxygen content in the insulation layer of the cold box of the air separation unit had increased. It was judged that there is a small amount of oxygen leakage, but not enough to warrant further attention. On 12th July, cracks appeared on the outer surface of the cold box, and the amount of leakage further increased. But the ASU continued to operate due to the high oxygen demand on the gasification plant.

The sequence of events resulting from the liquid leak into the coldbox is clear, but the events which caused that leakage are still not determined and the report states that "the specific cause of the accident is under further investigation."

However, the report also makes some very pertinent recommendations, such as ensuring that organic matter control in the air at the inlet of the compressor is in place. It also recommends that the hydrocarbon content of the liquid oxygen system must be regularly and accurately measured.

These points might cast some minds back to the horrific ASU explosion that took place at the Gas-to-Liquids (GTL) plant in Bintulu, Malaysia in 1997.

Learning the lessons

Gasification processes require vast quantities of oxygen and some of the world's largest ASUs are associated with the gasification of refinery heavy residue, coal and natural gas.

> "Looking at the images of the devastated ASU site remind us that the hypothetical situation can, and does, occasionally become the tragic reality"

The Bintulu ASUs were installed to feed partial oxidation (POX) gasification reactors in a sophisticated GTL plant which produces transportation fuels, waxes and resins from natural gas. The ASU that stands at the site today is rated at 3,200 tonnes per day (tpd) of oxygen: what we might call a 'mega ASU'. ▸

In 1997 there were forest fires on the Island of Sarawak, where Bintulu is located. The smoke contained soot particles which accumulated in a cryogenic liquid oxygen reboiler on one of the ASUs[2]. By coincidence, in the same year an ASU at the Fushun Ethylene complex which made oxygen to convert the ethylene to ethylene oxide suffered a similar explosion. In this case, the root cause was traced back to abnormally high ethylene levels in the ambient air due to shutdown venting on the ethylene plant[3].

In both cases, the combination of liquid oxygen, combustible hydrocarbon material and aluminium used to construct the reboiler led to a massive explosion and fire. Lessons from Bintulu, Fushun and one other ASU reboiler explosion have been captured in the EIGA doc 65/13: *Safe operation of reboilers/condensers in air separation units*.

Putting it into practice

Shin Tsushima, Vice-President, ASU Engineering for Matheson Tri-Gas in Texas, is a member of the CGA Yima incident investigation taskforce. He sets the ASU cryogenic safety scene in a very pragmatic way.

"The principal precautions against hydrocarbon contaminant build-up in the cryogenic liquid in the ASU are well established and focus on carbon dioxide analysis at the warm end of the ASU and hydrocarbons analysis in the cryogenic liquid oxygen sump," he explains. "Analysis of carbon dioxide (CO_2) after the pre-purification unit (PPU) is important to ensure that this gas does not enter the ASU, because it solidifies and causes blockages. Furthermore, detection of carbon dioxide break-through from the PPU is used to warn about the possibility that hydrocarbons such as methane or ethane are not being removed by the PPU and are also entering the ASU. This serves as an early warning system."

> "This enhanced laser technique is capable of accurate trace hydrocarbon measurements in a complex background gas matrix"

"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) analyser or an analyser that can detect individual hydrocarbon contaminants such as methane, ethylene, ethane and propane."

And, according to the EIGA document cited, additionally, for ASUs that use reversing heat exchangers at their warm end, routine analysis of acetylene in the liquid oxygen from the main reboiler sump is also required.

Reliable gas analysis is the key

Speaking as Head of Product Management for the continuous gas analyser product range within ABB's Measurement & Analytics business line, Steve Gibbons says, "Our experience is that between 10 and 15 gas analysers will typically be found in an ASU instrumentation shack with a handful more being required for the production of high purity argon."

"We observe that non-dispersive infrared (NDIR) analysers are a common instrument choice to measure CO_2 break-through from the PPU unit. Most of the time these analysers don't have much to do because there should be no CO_2 break-through detectable on the instrument."

"However, speed of response is important because an alarm is generally set at only 1 VPM of CO_2 to warn the operators that the PPU beds are saturated. And, since this measurement is related to operational performance and process safety, reliability is essential. When the analyser is reading zero for a long period of time, it is difficult for the operator to know if it is really working. But we can supply gas-filled cuvettes inside our Uras26 NDIR analyser so that it can frequently run an automatic test and calibration sequence. This provides the surety that the instrument will respond when needed."

For the THC measurement, many instrument engineers and plant operators will be familiar with flame-ionisation-detector (FID) gas analysers. 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 gas grades of high purity hydrogen and instrument air for its operation to create the flame. Cylinder changeovers of these consumable gases are required in addition to occasional calibration using a certified specialty gas mixture."

Innovative instrumentation

Gibbons comments that ABB has a range of established and innovative solutions in this area.

"Our FIDAS gas analyser has been used on many ASUs for decades and it is trusted by operators and plant builders worldwide. For THC or NMHC measurement it is a tried and tested option. However, for 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."

Regular acetylene analysis can be performed by taking liquid oxygen samples and sending them to a specialised accredited offsite contract laboratory. As instrumentation technology has advanced, ABB is confident that it has an innovation that is relevant for this application. "Most operators are looking to detect acetylene at less than 0.5 VPM," says Gibbons.

"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 enhanced laser technique is capable of accurate trace hydrocarbon measurements in a complex background gas matrix."

As a bonus, both innovative instrumentation techniques above require no consumable gases and have minimal calibration gas mixture requirements. This simplifies gas analyser maintenance and reduces their cost of ownership. These minimal intervention solutions are ideal where remote process control centres are located far away from the physical equipment. It all adds up to safe and productive ASU operations. gw

© ABB

REFERENCES

1. www.mem.gov.cn/gk/tzgg/tb/201907/t20190726_325359.shtml

2. Investigation of an air separation unit explosion. van Hardeveld, RM; Groeneveld, MJ; Lehman, J-Y; Bull, DC. Journal of Loss Prevention in the Process Industries, Volume 14 (3) – 1st January 2001

3. Investigation of the Fushun ASU explosion in 1997. Lehman, J-Y; Wei, XC; Hua, QX; Delannoy, G. Journal of Loss Prevention in the Process Industries, Volume 16 (3) – 1st May 2003