

## BY YEETIONG KOH

The dramatic growth of the ethylene market - reaching 200 million tons globally by 20201 - relies heavily on Asian production capability and capacity. Approximately half of the world demand for ethylene is for the manufacture of polyethylene, but it is also used to make vinyl chloride, ethylbenzene and many other valuable intermediate products such as ethylene oxide, ethanol ethylene oxide and ethanol. Ethylene has stringent purity requirements that must be verified in production and at custody transfer points as the presence of impurities can poison catalysts and affect downstream processes, leading to costly repairs and downtime. Measurement of purity directly impacts the bottom line.

The criticality of ethylene purity analysis means that the precision and reliability of the measurement is, of course, paramount, but speed and cost reduction are also important to prevent potential process upsets and to assure optimum throughput. The faster a reliable purity measurement can be achieved, the greater the product to market. For this reason, any significant advance in ethylene purity analysis that promises to lower costs and increase speed without sacrificing accuracy can have a major impact on the profitability of ethylene production plants. Such an advance is represented by the introduction of new quantum cascade laser (QCL)/ tunable diode laser (TDL) technologies

for ethylene analysis. Since the current technologies used for measuring gas purity both in production and custody transfer are reliable but relatively time consuming, the use of laser spectroscopy for measuring gas components has been a subject of interest for some time. Limitations in the technology, however, made it largely an experimental issue - until recently. The problems arising have been due to the fact that in spectroscopic laser gas analyzers, the external path that the light travels prior to entering the measurement cell can cause interference when the gas of interest is also present in the atmosphere, as is the case in the product purity measurement point of ethylene manufacturing.

Ethylene producers must certify that their product meets specification, but atmospheric moisture or carbon dioxide, for example, can negatively impact the measurement. The interference of atmospheric gases is conventionally dealt with in such ways as purging the laser path with nitrogen or scrubbed air to reduce the presence of the analyte in the analyzer housing, but these tactics make the use of the laser cumbersome and inappropriate for real-time use. In other words, no improvement on current technologies, o

The potential of laser technology for gas purity analysis has finally been realized in a multi-component hybrid QCL/TDL gas analyzer that has been developed to remove the external light path by using a novel zero gap design. By reducing the external path length to < 1mm, the spectrum arising from it can be almost entirely interferencefree as ambient air has minimal effect on the measuring spectrum. Compared to an analyzer with an external path length of 0.5m, this is a reduction of a factor of 500 for the traverse of the light path. This practically eliminates any spectrum from the external light and enables detection of sub ppmy levels of H O, CO, and other gases present in the atmosphere without the requirement to purge the analyzer housing. This new approach makes laser technology a real solution in industrial gas purity measurement for the first time.

While the new zero gap design has made laser technology viable for ethylene purity measurement, other advances have made it the preferred approach. QCL/TDL lasers are semiconductor instruments that produce light in the mid-IR range at a desired wavelength and use a laser chirp technique to scan a spectrum. To start the process, the laser is pulsed with electrical energy and heats up. The wavelength of the emitted light increases proportionally with the increase in temperature. A spectrum of one to three wavenumbers is scanned during the duration of a laser chirp, approximately one microsecond. Then the concentration of analytes can be calculated by converting the raw detector signal into a spectrum. Many thousands of spectra can be collected in just a few seconds since QCL/TDL lasers can be chirped at up to a 100 kHz frequency, and processing these spectra provides a strong signal with a good signal-to-noise ratio. The wavelength region that is scanned is selected to enable measurement of the desired analytes and it is often possible to detect more than one compound with a single device. An advanced signal processing procedure enables real-time validation of measurements and greatly reduces the need for calibrations. The results of this

multicomponent detection and real-time speeds means ethylene manufacturers can use laser gas analyzers for real-time process control and certify their product in real time by measuring all the components of interest in a single analyzer.

QCL/TDL systems can include up to six high-resolution lasers to measure both the near- and mid-infrared spectral regions for real-time, optimal gas measurement and analysis down to sub ppm concentrations. The ability to combine multiple lasers/ detectors in a single analyzer, covering the mid- and near-IR ranges, gives a versatile and configurable analyzer the ability to meet the measurement requirements for a range of different applications, and the ability to replace multiple incumbent analyzers with a single compact system which can reduce costs for ethylene measurement by eliminating the upfront price of multiple analysis systems without compromising accuracy. In fact, it can be improved.

The significant improvement in response time is a function of the fact that in a QCL/TDL the sample flows through a measurement cell where laser beams analyze the gas continuously. As a result, the response time is generally less than 10 seconds to get to 90 percent of a step change, so the output is essentially real time and continuous, a capability not possible before in gas purity analysis.

One of the principal applications for the QCL/TDL is in the final purification step which is made in an ethylene fractionation tower, or splitter. To ensure that production is on-spec, it's important that analysis is conducted for process control of the fractionator. It can be difficult to separate ethane and ethylene because they have similar physical properties. must maintain a very careful balance in their process control in order to keep ethane close to the specification limit without verging off-spec or recycling ethylene. Efficient operation of the tower minimizes energy consumption, avoids ethylene recycling, and decreases product giveaway, maximizing catalyst lifespan and performance to provide significant economic benefits. When plants measure the C1 and C2 molecules, as well as CO and CO2, as is possible with the QCL/TDL, the tower operation reaches optimum efficiency to ensure on-spec ethylene production.

Another application is the monitoring of the conversion in acetylene converters. In the acetylene converters, some molecules can be over-cracked and converted to acetylene during the cracking process. To maximize production, it is important to



convert this acetylene back into ethylene. This can be accomplished by adding hydrogen in catalytic beds called acetylene converters. There are two acetylene converters used - one in service and one on stand-by. To optimize acetylene conversion to ethylene and prevent process excursions, it's important to collect analytical data at the inlet stream, mid-bed, and outlet streams. To ensure the maximum amount of ethylene is produced, extremely accurate and rapid control of the catalyst is absolutely critical. If the catalyst is too active, some ethylene could be converted back to ethane, but if the catalyst is not active enough, not all the acetylene will be converted to ethylene. To control catalyst activity, it is essential to measure CO, as well as monitoring the concentration of acetylene to prompt the change from the in-service to the standby unit. To prevent process excursions downstream, it is also key to look for acetylene breakthrough at the outlet of the converters. Measurement of the outlet must be fast and with a low detection limit, so QCL/TDL is an ideal solution for this application as well.

For ethylene manufacturers throughout Asia, the QCL/TDL technology promises the first real-time gas purity measurement that allows one system to be used where multiple devices were previously required, reducing costs and footprint in ethylene plants.

<sup>1</sup> IHS Chemical, http://media.corporate-ir. net/media\_files/IROL/11/110877/05\_Global\_ Ethylene\_Market\_\_\_Outlook\_Eramo.pdf

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