

Specialty Gases for  
Hydrocarbon Processing



# LNG production



**Specialty gases are used in many of the unit operations in LNG production. Here are some examples.**

## Condensate separator

Natural gas flows from the seabed to a phase separator where solids, water, condensate and gases are separated. The composition of the condensate and gas phases coming off the phase separator are measured accurately to assess the type of gas coming from the well and ensure that the process parameters are adjusted accordingly. The CO<sub>2</sub>, hydrogen sulphide, water and methane content in gas are critical measurements. The analysis uses a highly accurate gas chromatograph with an FID or TCD detector. Gas chromatography can identify and quantify the concentrations of the components in the process streams.

A carrier gas such as Helium 5.0 grade, or Hydrogen 5.0 grade will be chosen for the chromatography. If an FID detector is used, there will be additional requirements for Hydrogen 5.0 grade and Zero Air to create the detector flame. The gas chromatograph is calibrated using a gas mixture containing similar components to the process

stream that is to be analysed. For custody transfer applications, a certified gaseous standard reference material accredited to ISO 17034:2016 is required.

## Amine sour gas sweetening

Sour gas sweetening using amine units is essential so sulphur levels in natural gas are low to ensure the product will burn cleanly in houses and other industrial applications. H<sub>2</sub>S also reacts with moisture to form corrosive acid which would destroy the gas distribution pipework.

The lead acetate tape method is favoured for process control of the amine gas sweetening units. Calibration of this instrument is usually conducted every three months with the introduction of a high precision calibration mixture containing a known concentration of H<sub>2</sub>S at approximately 60% of the full-scale deflection on the instrument, so a certified calibration gas mixture of 5 ppm H<sub>2</sub>S in nitrogen is ideal.

## Glycol dehydration

Moisture removal is essential for many reasons. Firstly, it would form ice in the LNG liquefier and block the pipework. Moisture also reacts with SO<sub>2</sub> or H<sub>2</sub>S, which may be present in the natural gas in very small quantities. The resultant acids would attack the pipework and cause leaks. Furthermore, moisture reacts with CO<sub>2</sub> and hydrocarbons to form hydrates that can block pipes and cause flow restrictions to vital instrumentation and valves.

The target moisture content in the natural gas at the outlet is around 1 ppm. Continuous, on-line moisture measurement at critical points in the process is essential to ensure successful processing and efficient, reliable plant operation. Measurement will typically be with an impedance moisture sensor. Calibration of the instrument during operation can be achieved with a certified calibration gas mixture containing 1 ppm of moisture in nitrogen.

## Mercury removal unit

Mercury levels in natural gas can range from less than detectable to approximately 10 ppb by volume. Mercury is removed in the MRU using a molecular sieve to avoid problems in the subsequent cryogenic

liquefaction unit. Mercury at the outlet of the MRU can be measured using cold vapour atomic absorption spectrometry (CVAAS). The instrument requires high purity instrument grade air as a carrier gas. Another popular technique for online mercury analysis in the petrochemical industry is atomic fluorescence which follows the ASTM 6350-98 and ISO 6978-2 procedures. This technique requires the use of either Argon 5.0 grade or Nitrogen 5.0 grade as a carrier gas. Both methods can be calibrated using a mercury generator system.

## LNG liquefaction

The final unit operation is cooling of the gas stream to create liquefied natural gas at -162 °C. In addition to the production of LNG, additional liquids are produced such as LPG and some heavier C<sub>5</sub>+ hydrocarbons. The liquefier uses hydrocarbons that are produced within the process as refrigerant gases.

**Bespoke sourcing of high purity hydrocarbons for liquefaction train start-up is a highly specialised service with which the Coregas specialty gases team have valuable experience and a highly successful track record.**

### Australia – the lucky country

Australia is gifted with a diverse range of primary resources from minerals to oil and gas. A wealth of energy reserves lies hidden under our soil and in our oceans. Through careful extraction and processing, these reserves can be converted to valuable fuels to drive our local economy and for export to our trading partners overseas. Australia is the world's number two LNG exporter worldwide: only Qatar exports a higher tonnage of LNG per year.

# LPG production

LPG is a mixture of propane and butane. These relatively light hydrocarbons are produced either from 'wet' natural gas sources which contain these molecules in addition to the lighter methane and ethane molecules or during the refining of crude oil, where they are among the lightest fractions recovered.

An LPG fractionation processing facility may include the following unit operations, each requiring a range of specialty gases.

## Tanker terminal

Knowledge of the incoming raw material is essential for production planning and process control. For transfers between operators, it is also the critical measurement for billing according to the product composition and associated financial value. Gas chromatographs fitted with TCD or FID detectors are the most common analytical equipment to use for this composition analysis. High purity specialty gases such as Helium 5.0 grade, Hydrogen 5.0 grade and Zero grade Air re used as carrier and detector gases for this instrumentation. Accurate calibration gas mixtures blended at a target composition to reflect the typical incoming feed stream are also required.

## Pre-fractionation heaters

Combustion of ethane produces the energy required to heat up the incoming feed material and allow the distillation processes to function. Burner combustion control calibration gas mixtures are used to ensure that the air/fuel mix in the burner is correct to achieve good stoichiometry. This maximises energy efficiency and minimises emissions. Emissions monitoring from the furnace gases using CEMS also takes place to ensure environmental compliance.





### **Ethane, de-propaniser, de-butaniser and naphtha distillation columns**

Process control in the distillation columns relies on a combination of rapid response direct read temperature and pressure measurement, and chemical analysis using gas chromatography. Carrier gases, calibration gas mixtures and detector gases are required.

### **Propane & butane molecular sieve purifiers**

The molecular sieves become loaded with water and sulphur chemicals, so require periodic regeneration. The purified gases emitted from the molecular sieve purifiers are continuously analysed for moisture and sulphur content to ensure that the process is under control and that there is no breakthrough from the adsorbers. For rapid response to changes in the process conditions, online process control analysers such as a pulsed ultraviolet fluorescence (PUVF) instrument for total sulphur analysis will be used. Calibration gas mixtures containing ppm or low % levels of SO<sub>2</sub> are required.

# Biogas production



Biogas digesters, sludge digesters and gas collectors from landfill gas can be used to produce methane, which is then supplied to the natural gas distribution grid. Biomethane differs from natural gas in many ways. It is CO<sub>2</sub>-rich and methane-lean. It contains no higher hydrocarbons, so it is not so rich in energy as natural gas. Biogas may also contain traces of ammonia, siloxanes and halogenated hydrocarbons, which must all be removed prior to introduction into the natural gas distribution grid.

Monitoring of these impurities and measurement of biogas' methane and CO<sub>2</sub> content is critical to ensure a high quality product and reduce the risk of corrosion and potentially dangerous toxic gas leaks. An on-line gas chromatograph with TCD detector that can measure the biogas composition within a short (two to four-minute) cycle time is often used. Helium 5.0 grade is the most common carrier gas selected for this application, although Hydrogen 5.0 grade may also be used.

The calibration gas mixture for rapid response in the GC-TCD is a blend designed to match the biogas composition.

An ISO 17034:2016-accredited certified reference material should be specified to ensure traceable and accurate invoicing.

## Unparalleled expertise at your disposal

Our pedigree in specialty gases for hydrocarbon processing applications is unrivalled in Australia. For several decades, the Coregas team have been Australia's specialty gases experts. In our specialty gases production facility at Yennora NSW, we have more than 100 years of accumulated experience in our team of NATA-approved signatories for our ISO 17025 and ISO17034:2016 accreditations. Furthermore, our sales and customer service teams both have experts dedicated to specialty gases who assist with technical queries and offer product selection advice.



# Natural gas distribution



Some natural gas sources in Australia are liquefied for export to Asia as LNG. Others are distributed through the Australian natural gas pipeline network. The natural gas distribution grid receives inputs from these various sources and operates over 88,000 km of distribution pipelines to supply gas to more than 4.3 million households and 130,000 business customers.

## Heating value measurement

Natural gas may originate from biomethane, shale gas, coal seam gas or conventional natural gas. With so many inputs from different sources, each with different compositions, the natural gas distribution network is a cocktail of different gases. Some sources are rich in methane, while others contain additional higher hydrocarbons such as ethane, propane and butane.

To ensure sources to the grid are remunerated fairly and customers taking gas from the grid are paying the correct price for the energy they consume, there is regular metering of the gas for flow rate and measurement of its calorific value, also known as heating value.

Heating value measurement involves the use of a highly accurate GC-TCD or GC-FID

instrument. This analyser is calibrated using high precision synthetic natural gas reference materials, which are used to determine the heating value of the natural gas. The calibration gases are generally accredited to ISO 17034:2016. Use of a carrier gas such as Helium 5.0 grade for the chromatography is also essential. If the GC-FID setup is used, additional fuel gas (Hydrogen 5.0) and oxidant gas (Zero Air) will be required. There is no additional zero gas required, because the carrier gas doubles up as the zero, or reference, gas. There are no additional instrumentation gases required for the TCD detector.

The heating value and Wobbe index of the natural gas is calculated from the exact composition of the various hydrocarbons that the gas stream contains using the mathematical formulae in ISO 6976:2016.



## Pipeline integrity

Sources of natural gas are purified to remove water, mercaptans and hydrogen sulphide. These chemicals can cause corrosive acids that might cause corrosion of the gas pipelines. To ensure the water and H<sub>2</sub>S levels in the pipeline are at suitably low levels, they are measured using analytical instrumentation or electrochemical gas sensors. These devices require calibration and testing with specialty gases mixtures that contain very low concentrations of water or hydrogen sulphide (circa 5 ppm) and a zero gas such as Nitrogen 5.0 grade.

One of the highest risks for natural gas pipelines is air ingress, which is detected by measurement of oxygen levels in the pipeline. The analysis of oxygen is done using a paramagnetic oxygen analyser, which is calibrated using either air or a certified calibration gas mixture containing a known concentration of oxygen in nitrogen. The instrument also requires a zero gas such as Nitrogen 5.0 grade. The desirable measured oxygen concentration is less than 0.1%. Any level approaching 2% would be indicative of a serious failure and would trigger an alarm.



# Gas detection



In hydrocarbon processing, gas detection is essential. A range of flammable gases are often present and some toxic gases such as hydrogen sulphide or BTEX chemicals may also present a hazard. The gas detection equipment in chemicals plants is often fixed in locations where it is perceived that a leak might be most likely, for example over a valve or near a compressor. Portable gas detectors, worn as PPE, are also common. These detection sensors require testing and calibration with specialty gas mixtures.

When entering storage tanks for maintenance or cleaning, the operator works in a confined space where the free flow of air may not be possible. The space may also contain residual vapour from various chemicals previously stored in the tank or nitrogen gas from purging activity. Gas detection PPE should be worn to give notice of any gas risks.

Typical gas mixtures for testing and calibration of gas detectors on refineries include:

- 1.25% methane, 25 ppm hydrogen sulphide, 100 ppm carbon monoxide, balance air
- 2% hydrogen, balance nitrogen
- 25 ppm sulphur dioxide, balance nitrogen
- 50 ppm ammonia, balance nitrogen

## Quality levels for gas detection gas mixtures

Quality requirements for daily use functional test gas mixtures (bump test gases) are generally not as high as gas mixtures used for detector and sensor calibration. For functional test gases, an ISO 17025-accredited gas mixture might be specified.

For the quarterly, half yearly or annual calibration of the gas detector sensors, an accredited calibration gas mixture is required. For the highest levels of measurement confidence and traceability, it is necessary to use an ISO 17034:2016-accredited reference material.

Note that under the correct usage and interpretation of the ISO 17034:2016 standards for reference material producers, each individual cylinder must be prepared and validated for stability and homogeneity. It is therefore not possible to decant fill ISO 17034:2016 reference materials from a large mother cylinder to smaller portable disposable types, or one-time use cylinders and declare the smaller cylinders as also being ISO 17034:2016 compatible, unless they are subsequently also individually analysed. However, this would consume a large proportion of their contents and is therefore not feasible.



# Specialist products

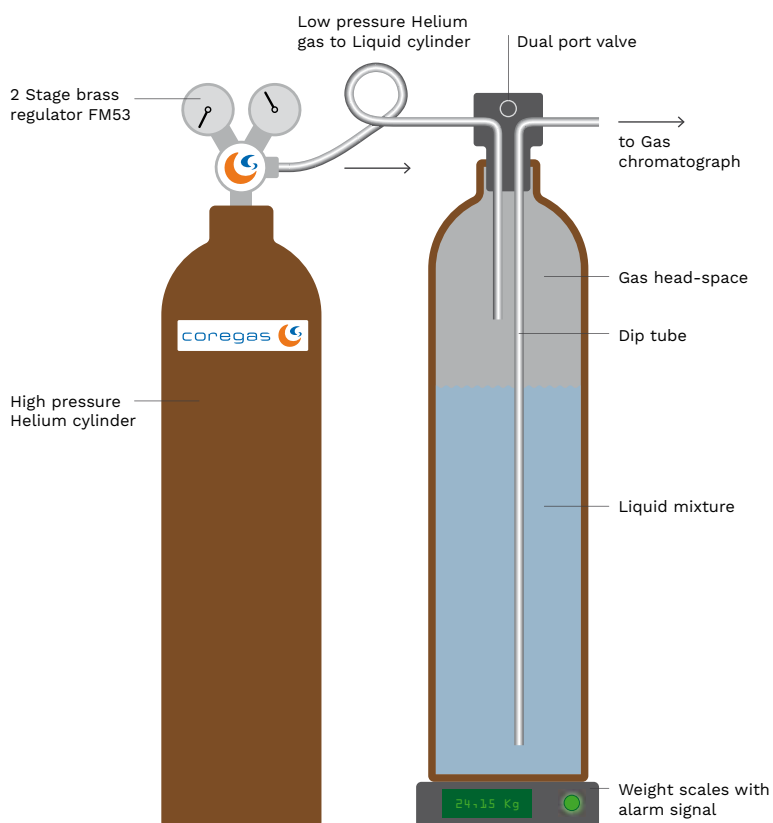


## Liquid hydrocarbon mixtures

In hydrocarbon processing applications such as crude oil refining, it is common to use liquid mixtures to calibrate analytical instrumentation. At Coregas, we have a broad range of hydrocarbons that can be used to produce liquid hydrocarbon mixtures in cylinders. A liquefied calibration gas mixture is maintained as a liquid in the cylinder with either the vapour pressure of the hydrocarbon components or with a head pressure of helium gas.

To ensure that the liquid phase sample is withdrawn from the cylinder a dip tube is fitted to a dual port cylinder valve. The bottom of the dip tube is immersed in the liquid at the bottom of the cylinder, therefore enabling withdrawal of the liquid phase from the cylinder.

When the liquid level falls below the dip tube, the product withdrawal from the cylinder will be from the gas phase. Furthermore, the cylinder must be kept in an upright position to ensure that the dip tube remains immersed in the liquid.



Liquid hydrocarbon blend usage

A supply of helium to the dual port valve gas side will allow continuous withdrawal of liquid. Helium 5.0 grade is ideal for this purpose. Since the pressure in the liquid cylinder remains constant using the helium to pressurise it, the cylinder pressure will not fall as the contents are depleted. The easiest way to determine the cylinder contents is to mount the cylinder on a weighing scale. An alarm can be set when 50% of the mixture has been used to ensure timely re-ordering of a replacement cylinder.

### Portable calibration gas cylinders

We offer a wide range of CEMS calibration gas mixtures and gas detection calibration gases in our ultra-portable calibration gas cylinders. Each gas mixture is available in our 100 or 116 litre sizes for extended usage life. The product shelf life varies according to the reactivity of the gas mixture, but for most products we guarantee two or three years of stability.

Speed is often of the utmost importance for delivery of portable cylinders, so we stock the most popular products for dispatch within just a few days of receiving your order. Additional products can be made to order and will take just a little longer to prepare for you.

At Coregas, we believe in a sustainable approach to doing business. That is why our portable range of calibration gas cylinders comes with a full return service offer, so that you have no issues with disposal of the packages after use.

## Made in Australia

The range of specialty gases that Coregas can offer to various hydrocarbon processing operations are Australian to the core. We produce ingredients for many of them at our air separation unit located in Port Kembla. From those pure gases, we then fill a range of high purity gases or gas mixtures in cylinders in our highly specialised laboratory in Yennora. From this location, near Sydney, we transport the gas cylinders to locations across the country.



# Typical calibration gas mixtures



## BTEX calibration gas mixtures

There are many different volatile organic compounds (VOC's) that may be present in the air around petrochemical facilities. Four that are commonly measured together are referred to as BTEX. They are:

- Benzene
- Toluene
- Ethylbenzene
- Xylene

Calibration gas mixtures with these VOCs are often required at the following concentrations:

- 100 ppm for gas detectors used in refining, petrochemical processing and petrochemical tank storage operations
- 1 ppm for air quality monitoring, for example perimeter monitoring in the petrochemical sector or by environmental scientists

## CEMS calibration gas mixtures

The acronym CEMS refers to continuous emissions monitoring systems, which are on-line analysers that accurately measure the pollutant gases emitted from static industrial sources or power generation plants. To ensure measurement accuracy, CEMS instruments require periodic calibration with high precision, traceable specialty gases calibration mixtures.

Typical CEMS calibration gas mixtures include:

- 100 ppm CO, balance Nitrogen
- 100 ppm NO<sub>x</sub>, balance Nitrogen
- 100 ppm SO<sub>2</sub>, balance Nitrogen
- 10 ppm Ammonia, balance Nitrogen

## Process control gas mixtures

The number and diversity of calibration mixtures used for process control is infinite. At Coregas we can make mixtures to order according to your specifications. This means that you get precisely what you need, and we will always go the extra mile to make sure that you get it exactly when you need it.

The most common quality level for process control gas mixtures is to use ISO 17025-accredited gas mixtures. Certified reference materials with ISO 17034 accreditation are

also suitable for process control applications but the extra precision, traceability and cost is not always required.

In addition to a span gas, most process control instrumentation will require a zero gas such as Nitrogen 5.0 grade or Zero Air. If chromatographs are used for process control applications, a carrier gas such as Helium 5.0 grade or Hydrogen 5.0 grade will be needed.

## Process control calibration gas mixtures

**Here are a few examples of typical process control calibration gas and liquid mixtures from various chemical processing applications:**

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Natural gas amine treatment for sweetening (H<sub>2</sub>S removal), eg lead acetate tape analyser calibration

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- 5 ppm H<sub>2</sub>S balance Nitrogen
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Natural gas dehydration (water removal in adsorber or glycol scrubber)

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- 1 ppm H<sub>2</sub>O balance Nitrogen
  - 10 ppm H<sub>2</sub>O balance Methane
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Sulphur recovery SCOT process final clean up (SO<sub>2</sub> removal), eg UV fluorescence analyser calibration

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- 50 ppm SO<sub>2</sub> balance Nitrogen
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Total sulphur measurement in crude oil refining (crude assay or product control), eg PUVF analyser calibration

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- Various mercaptans with total sulphur content at 50 ppm in other liquid or gaseous hydrocarbons
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Continuous catalyst regeneration (CCR) unit nitrogen purge process control, eg TCD analyser calibration

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- 1% hydrogen balance Nitrogen
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Catalytic steam methane reformer for hydrogen production final product purity control, eg TCD analyser calibration

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- 5% CO balance hydrogen
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SCR NO<sub>x</sub> reduction ammonia slip control, eg FTIR analyser calibration

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- 10 ppm Ammonia balance nitrogen
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SCR NO<sub>x</sub> reduction DeNO<sub>x</sub> process control, eg chemiluminescence analyser calibration

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- 10 ppm NO<sub>x</sub> balance Nitrogen
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FGD - SO<sub>2</sub> scrubbing process control, eg SO<sub>2</sub> PUVF analyser calibration

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- 100 ppm SO<sub>2</sub> balance Nitrogen
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Amine treating process for flue gas CO<sub>2</sub> recovery, eg NDIR analyser calibration

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- 5% CO<sub>2</sub> balance Nitrogen
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Combustion control flue gas oxygen measurement, eg zirconia oxygen sensor calibration

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- 8% Oxygen balance Nitrogen
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Combustion control flue gas CO measurement, eg NDIR instrument calibration

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- 500 ppm CO balance Nitrogen
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# Gas control equipment



Process control gas instrument calibration span gas mixtures are used for short term calibration events. If the operator is in attendance for the calibration, they may make any required adjustments to the regulator outlet pressure. So these applications are suitable for single-stage cylinder pressure regulators. If the calibration is automatic and remote, then a two-stage automatic changeover panel, which allows continuous supply of gases as a depleted gas cylinder switches over to a reserve cylinder, is recommended.

Whether you specify chrome-plated brass or stainless steel depends on the components in the calibration gas mixture. For fully inert components, chrome-plated brass is suitable. If the mixture contains any traces of corrosive gases such as mercaptans, ammonia, or oxides of sulphur or nitrogen, then upgrading to a stainless steel regulator is essential to preserve the precise certified composition of the calibration gas mixture.

In addition to a span gas, most instrumentation requires a zero gas such as Nitrogen 5.0 grade or Zero Air. Single-stage chrome-plated brass specialty gases regulators are suitable for these gases if used in clean environments.

Instrumentation gases and gas mixtures, such as helium for gas chromatography or hydrogen and air for FID flames, are continuous flow applications. In these situations, the use of a two-stage regulator is essential to ensure a stable gas supply pressure as the content of the cylinder is depleted. Better still is the use of a two-stage automatic changeover panel, which allows continuous supply of gases as a depleted gas cylinder switches over to a reserve cylinder.



In all cases above, if the regulators are used offshore where salt water sea spray exists or in refineries, natural gas processing facilities or biogas production facilities where H<sub>2</sub>S is generally present in the air, then a stainless steel regulator is recommended.

Our specialty gases customer service and sales teams would be pleased to assist with your process control zero and span gas mixture requirements and make a proposal for the most appropriate gas pressure regulator. Coregas is Australia's only supplier of the Spectron range of gas control equipment, the perfect range to accompany our high precision calibration gas mixtures.

### Full range of industrial gases

The oil and gas sector, with downstream operations in refining, gas processing and distribution, has frequent requirements for a wide range of industrial gases. Welding gas mixtures are used daily for construction, maintenance and repair operations. Bulk scale supply of pure nitrogen gas is essential for a range of inerting, purging and blanketing operations to ensure safe pipeline use and product storage. Bulk supplies of hydrogen and oxygen as reagents in hydrocarbon processing chemical reactions are also within our scope. Working with Coregas makes things easy: all these products, and Australia's most up to date range of specialty gases, are available to you from just one supplier.





### **Proudly Australian**

Coregas operates in Australia and New Zealand supplying a range of industrial, medical and specialty gases to our market. We are a member of Wesfarmers, one of Australia's largest companies. Wesfarmers is the largest private employer in Australia and its profits are recycled into the Australian economy.





## Specialty gases for hydrocarbon processing

LNG, LPG, biogas, refining and petrochemical production: the hydrocarbon processing industry is the most diverse of all the sectors that Coregas serves with specialty gases and related gas control equipment. Applications include: high purity gases for laboratory analysers; accredited calibration gas mixtures for emissions monitoring and process control; bump test gases for gas detection safety equipment and high precision gas control equipment to deliver your gases securely from the cylinder to your point of use. No other sector that we serve has such a diverse and fascinating range of requirements, and we have invested many years in developing our product range and expertise to serve the needs of this industry.

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