

INDUSTRIAL GASES

This article describes the uses and production of five gases (acetylene, hydrogen, carbon dioxide, nitrogen, oxygen and argon)

Acetylene is made by the reaction of calcium carbide with water; hydrogen is made by the electrolysis of water; carbon dioxide is obtained from Kapuni gas; nitrogen, oxygen and argon are obtained from air by fractional distillation. .

INTRODUCTION

This article describes the production of five gases (acetylene, hydrogen, carbon dioxide, nitrogen, oxygen and argon) by BOC Gases (NZ) Ltd. The products are all gases under normal conditions, but are not necessarily stored or transported as such.

Uses of industrial gases

The different gases are used in a wide variety of industries, but most notably in the metal, polymer and food industries. Uses of the individual gases are discussed below.

Acetylene

Acetylene is mainly used in oxy-acetylene flames for cutting mild steel and for welding.

Hydrogen

A small proportion of the hydrogen is used by BOC Gases to react with traces of oxygen in other gas streams. The two gases react forming water, which can be easily condensed out of a gas mixture. The majority of the hydrogen is sold to the edible fats and oils industry where it is used to hydrogenate vegetable oils to make margarine (see article VI-G).

Carbon dioxide

Carbon dioxide is used widely in the food industry for applications such as removing the caffeine from coffee beans to make decaffeinated coffee and for carbonating beer, soft drinks etc. It is also used for cooling in the food and manufacturing industries.

Nitrogen

Nitrogen has two main uses: cooling and as an inert atmosphere. As liquid nitrogen it is used for cooling in many industrial processes and in the food industry. As gaseous nitrogen it is used to form an inert blanket over substances that would otherwise be oxidised by the air. Nitrogen is used for cooling various mechanical equipment that needs to be kept extremely cold and for snap-freezing foods such as chicken, hamburger patties and fruit to be eaten out of season. Inert blankets of nitrogen are used over reactive liquids in tankers, in varnish manufacture and also inside potato chip packets.

Oxygen

The majority of the oxygen produced by BOC Gases is used by the Glenbrook steel mill to oxidise unwanted impurities in the steel. The remainder is in the food industry, for medical oxygen for respiration and in oxy-acetylene torches.

Argon

Argon is highly unreactive and so, like nitrogen, can be used as a protective blanket to prevent substances from oxidising. Argon is mainly used to protect very hot metal, as this is highly reactive. Most of it is used in welding to protect the molten metal, and a small amount is used in light bulbs to prevent the white-hot tungsten filament from oxidising.

BOC Gases also distributes a variety of other gases including compressed air.

THE MANUFACTURING AND PURIFICATION PROCESSES

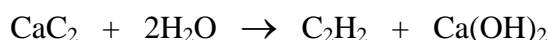
The acetylene and hydrogen manufacturing processes are covered below. The carbon dioxide is bought in liquid form from the Kapuni natural gas plant (where it is a by-product of their process, see article VII-C). Nitrogen, oxygen and argon are all extracted from the fractional distillation of air, so these gases are all covered together. Overall figures for purity and production capacity are given in **Table 1**.

Table 1 - Gas production statistics

	Purity/%	Contaminants
Acetylene	99.5	Traces of air Low levels of NH ₃
Hydrogen	99.999	O ₂
Carbon dioxide	99.98	Traces of air and hydrocarbons
Nitrogen	99.999	Ar, O ₂
Oxygen	99.5	N ₂ , H ₂ O, Ar, CH ₄
Argon	99.999	N ₂ , O ₂ , H ₂ O

Acetylene

Acetylene is manufactured by the action of water on calcium carbide:



A sealed hopper is kept filled with crushed calcium carbide (imported mainly from Norway) and a slow moving worm carries the solid forward to fall into a three metre high reaction vessel (**Figure 1**). The reaction occurs spontaneously on mixing and the gas formed passes *via* a hydraulic main to a gas holder where it is stored above water. The addition of water to the reaction vessel is regulated manually. If the gas production becomes too rapid the reaction is slowed by the addition of more water, which lowers the temperature and hence the rate. The acetylene flows from the gas holder through a series of trays containing mainly ferric chloride to remove impurities such as hydrogen sulfide, phosphine and ammonia.

The gas then passes through a drier containing calcium chloride. It is then compressed to 20

atmospheres¹ and passed through another bed of calcium chloride to remove the last traces of water. The compressed gas is then pumped into cylinders or tankers where it dissolves in acetone to ensure it can be transported and handled safely.

Calcium carbide

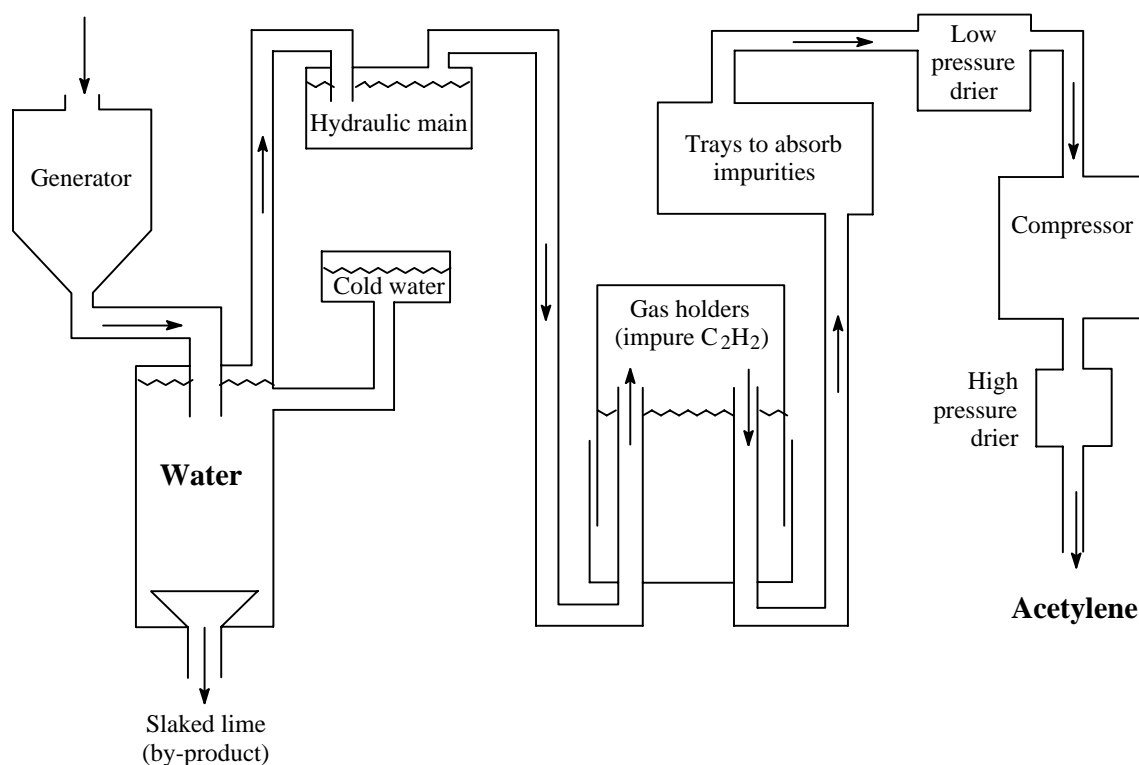


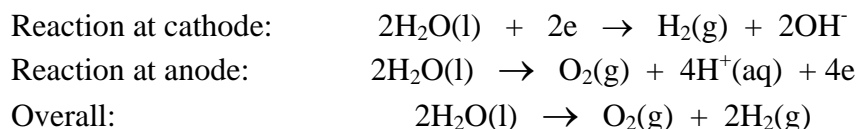
Figure 1 – Production of acetylene

The major byproduct from the process is slaked lime ($\text{Ca}(\text{OH})_2$). This is dewatered in a series of settling ponds then sent to a waste disposal company. Some of the lime is dumped but the majority is used for lowering the pH of effluent water.

Hydrogen

Hydrogen is manufactured by the electrolysis of water. The water used is first distilled and then passed through several ion exchange columns to remove any mineral contaminants. It is then pumped to electrolysis cells which containing potassium hydroxide. The hydroxide acts as an electrolyte so it is not consumed, so while the cells need to be continually topped up with water they only rarely need extra hydroxide.

The electrolysis occurs at low current but relatively high voltage in steel tanks with nickel-plated steel electrodes in a solution with a specific gravity of 1.225.



The two gases are collected in separate pipes. The oxygen is simply vented to the

¹If it is compressed any further the acetylene decomposes.

atmosphere, while the hydrogen is further treated. It is compressed to 172 bar and heated to 90°C (the compression alone heats it to about 70°C) and passed over a mixture of palladium and alumina. Any contaminating oxygen is catalytically reduced to water, but the gas is of a sufficiently high temperature to prevent this from condensing out and deactivating the catalyst.

The gas is then dried over a mixture of alumina and silica gel then passed through a gas filter, compressed and pumped into cylinders or tankers.

Carbon dioxide

Carbon dioxide is produced at Kapuni by the Natural Gas Corporation. and then sent to BOC Gases as liquid in pressurised tankers. In addition to selling it in liquid form some is converted into dry-ice, solid CO₂ which sublimates at atmospheric pressure at -78°C. (Sublimation is the process of a solid changing to a gas without going through a liquid form.) To make dry-ice the liquid is rapidly depressurised, causing some of the CO₂ to solidify and the rest to be vented as a gas. The gaseous fraction is collected and recycled for both economic and environmental reasons. The CO₂ 'snow' is then compressed into pellets and sold to industry.

The fractional distillation of air

Air is composed largely of nitrogen, with a significant amount of oxygen and traces of the noble gases and other compounds (**Table 2**). Nitrogen, oxygen and argon are separated on the basis of boiling point and any compounds that will interfere with the end uses are removed before distribution.

Table 2 - The average composition of air

	% by volume	boiling point / °C
Nitrogen (N₂)	78.08	-196
Oxygen (O₂)	20.95	-183
Argon (Ar)	0.93	-186
Carbon dioxide (CO₂)	~0.035	-78*
Neon (Ne)	0.00182	-246
Helium (He)	0.00052	-269
Krypton (Kr)	0.00011	-152
Xenon (Xe)	0.00009	-108
Hydrogen (H₂)	0.00005	-253
Nitrous oxide (N₂O)	0.00005	-88
Water (H₂O)	up to 4.0	100

*Carbon dioxide does not boil, it sublimates (i.e. goes from a solid to a gas without passing through a liquid phase). This is the sublimation point (rather than boiling point) of carbon dioxide.

The separation involves liquefaction of air followed by fractional distillation. Nitrogen (which has a lower boiling point) is more volatile than oxygen or argon. Water and carbon dioxide must be removed, and oxygen must be removed from the argon and nitrogen streams (as these are used as blankets to prevent oxidation) but the other constituents need not be because of their low concentration and inertness. Several important principles are involved in the process and are summarised below:

- When work is done on air, by compressing it, it becomes hotter.
- When compressed air is expanded through and opening or valve it becomes cooler.
- When air is expanded in a turbine it does work on the rotors and cools by approximately ten times as much as in simple expansion.
- When a mixture of liquids is in equilibrium with its vapour, the vapour above the liquid is richer in the more volatile component (i.e. more of the lower boiling liquid vapourises).
- The boiling point of a liquid is lower at lower pressure.

Liquefaction

Figure 2 shows the layout of a typical air liquifaction plant.

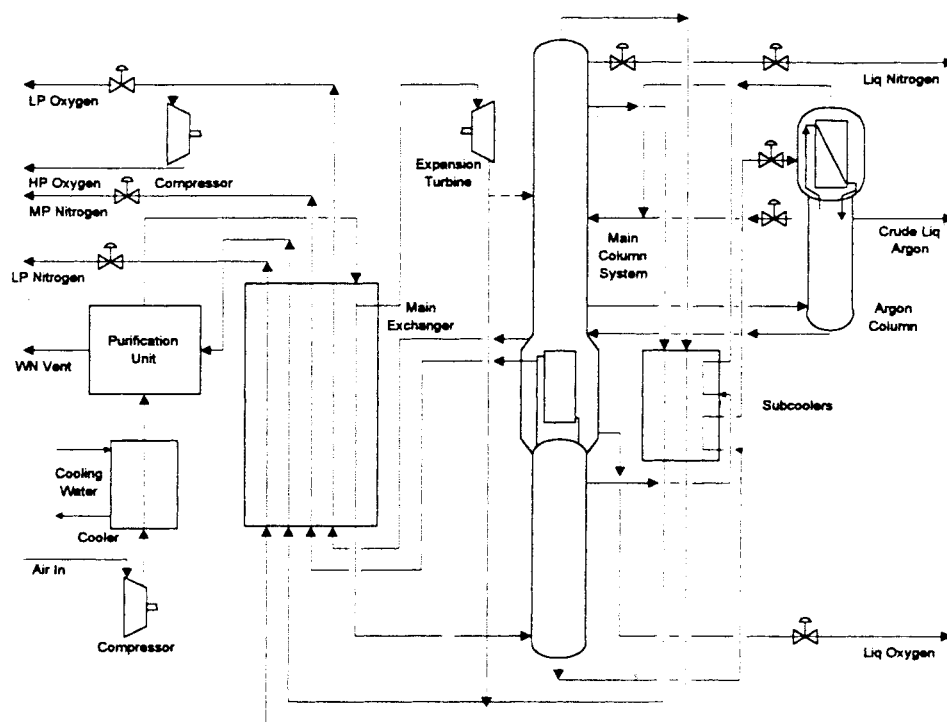


Figure 2 - Typical layout of an air liquifaction plant

At the BOC plant at Glenbrook air is drawn in from the atmosphere and passed through a series of compression stages which increase the pressure to about 6 atmospheres as isothermally as possible, the final temperature being $\sim 30^{\circ}\text{C}$. To keep the temperature down the air is passed through water coolers after each of the first three compression cycles. After the 5th stage the compressed gas passes through a direct cooler, i.e. it is in contact with the cooling water. It then passes through a reversible heat exchanger of a honeycomb design where the coolant, flowing in a different pipe and in the reverse direction, is cold nitrogen gas at -167°C and 0.5 atm pressure from the fractionating column. The temperature of the air at

the mid-point is $\sim -105^{\circ}\text{C}$ and -165°C when it emerges. During this process carbon dioxide and water vapour freeze out from the air stream on to the cold surface. To prevent these blocking the pipe the flow streams are reversed every 12 minutes, i.e. the cold nitrogen flows through the pipe that had carried the air stream and vice versa. The lower pressure nitrogen stream removes the ice and solids CO_2 .

This fully compressed air now enters the main heat exchange block. This block has pipes for several different gas streams. The coolants of this block are waste N_2 and O_2 from the fractionating column and 10% of the air stream which is taken from the near the bottom of the lower fractionating column. The 10% air stream emerging from the main heat exchanger passes through the expansion turbine and cools to -162°C by doing work on the rotor blades as it undergoes a pressure drop from 6 to 0.5 atm. This turbine drives a generator and power is returned to the national grid. This further cooled air then goes back to the reversible heat exchanger.

After passing through the heat exchangers the air is now cooled to just above the dew point and enters the bottom of the first and lower fractionating column.

Fractional distillation

The liquid air is fractionally distilled to separate the more volatile nitrogen from the less volatile oxygen according to the fourth principle mentioned earlier. The air separation unit

consists of two columns (lower and upper) in which a large number of successive distillations and condensations can be carried out on a continuous basis. The columns contain a series of horizontal metal trays, each containing a number of small holes and two drain pipes to the tray below. Liquid is held on the trays while vapour bubbles up through the holes with sufficient velocity to prevent the liquid dripping back. The vapour entering a tray from beneath is warmer than the liquid on the tray, with the result that some of the vapour condenses and some of the liquid vapourises and rises to the tray above.

The vapour evaporating from each tray is richer in nitrogen than is the liquid remaining. Consequently, as we proceed up the columns both liquid and vapour phases become enriched in nitrogen, while the oxygen concentration increases towards the bottom of the columns.

The lower column with ~ 25 trays operates at six atmospheres pressure and yields a liquid at the bottom at a temperature of -180°C containing 30 - 35% oxygen. This is run off, passed through an expansion valve causing a pressure drop to 0.4 atmospheres and run into the upper column with ~ 75 trays about two thirds of the way up. Almost pure liquid oxygen collects at the bottom of the upper column at -180°C . This liquid is divided by thin walls from the top of the lower column. Because the lower column is run at higher pressure this temperature is low enough to condense the gaseous nitrogen at the top of the lower column since at six atmospheres pressure the boiling point of nitrogen is -177°C (principle 5). Thus liquid nitrogen containing $< 10 \text{ vpm}^2$ oxygen is run off at the top of the lower column, and the heat exchanged causes oxygen vapour to rise up the upper column. Some of this liquid nitrogen is run off to storage while the remainder passes through an expansion valve into the top of the upper column. Gaseous nitrogen is continuously drawn off from the top of this column at

²10 parts of oxygen per 10^6 parts of nitrogen by volume

-193°C, used in heat exchangers as previously described and then discharged to the atmosphere.

The plant produces oxygen at very high purity, while a minor amount of the oxygen originally in the air goes to waste with nitrogen. If a single stage column were used, 40% of the oxygen would be lost.

Oxygen is then removed from the argon stream by Pd catalysed reaction with hydrogen, and then the moisture from this process is removed with alumina ready for cylinder filling.

Cylinder filling

Gases can be transported in cylinders as gas or liquid. All gases for lower volume industrial applications are despatched from BOC Gases in cylinders. These come in a variety of sizes from A (the smallest) to G (the largest). The cylinders are all colour coded for identification³. Before it is filled a cylinder to contain liquified gas is put onto very sensitive scales and filled through a valve until the correct weight is reached. Many applications require a mixture of gases (e.g. Guinness use a 1 : 4 carbon dioxide : nitrogen mixture to carbonate their beer) and these are calculated by adding the correct weight of one gas then the next. Once the cylinder is filled the liquid gas in the filling tube is vented off (to prevent it from expanding and destroying the tube) and the cylinder sealed. It is then daubed with soapy water so that the person filling the cylinder can easily see if it has any leaks. Cylinders containing compressed gas are filled to the required pressure.

Some gases stored in liquid form must be kept in heat-insulated cylinders and kept at low temperatures. e.g. N₂, O₂, Ar, air. As the density of a liquid is far greater than that of a gas much greater amounts can be stored and transported in the liquid form.

PLANT SAFETY

Great care must be taken around the hydrogen and acetylene plants to prevent fires, as these are both highly flammable substances. Stringent controls are maintained over sources of ignition and incompatible materials such as oil around the oxygen plant. In some cases metal tools are made of bronze (rather than steel) so that they don't give off sparks during use, cigarettes are not allowed and cell phones etc. must be turned off. In the acetylene plant there is also danger from the calcium carbide as it gives off a large volume of acetylene gas when wet so it must be stored in the complete absence of moisture.

³Gases of different grades (i.e. medical grade oxygen versus oxygen for oxy-acetylene torches) usually have the same composition. However, the cylinders are kept separate so that any contaminants within the cylinder are not transferred to gases to be used elsewhere. This is particularly important for oxygen as the cylinders used for welding often become contaminated with acetylene, and it is important that medical oxygen doesn't become contaminated with this. It is simpler to keep the bottles separate than to subject them to rigorous cleaning each time they are used. All bottles are recycled.

UTILITIES

The hydrogen plant and air separation require a large amount of electricity so the plant has its own small sub station to provide this.

ENVIRONMENTAL IMPLICATIONS

Gas production is largely an extremely environmentally-friendly industry. With the exception of acetylene and hydrogen production, the processes concerned produce no waste. In acetylene production the waste produced is lime, which creates a small disposal problem, but most of it is used in water treatment. The only waste in hydrogen production is oxygen, which is naturally present in air and so does not create a problem.

When the gases are used, again there is little environmental damage. Nitrogen, oxygen and argon are simply different fractions of air, so returning them to the air has no detrimental effect. Hydrogen is also present in air, and is harmless. Carbon dioxide and acetylene (which is burnt, giving off carbon dioxide and water) are of more concern, but still do not cause serious damage. Any carbon dioxide that doesn't form into dry ice pellets is recycled on site.

The only two areas of concern are energy consumption and the use, at Glenbrook, of large volumes of cooling water.

THE ROLE OF THE LABORATORY

The laboratory is involved exclusively in quality control testing. The laboratory is equipped with gas chromatographs, and FTIR spectrophotometer and analysers for oxygen and moisture. Samples of all gases are tested in one of the gas chromatographs to ensure that their composition is within the acceptable limits of the required composition, and the other tests are carried out as necessary.

Depending on the grade a bulk batch of gas may be analysed, or the composition of each individual cylinder determined. The latter is used for the highest quality grades and for low volume special mixtures of specified composition required for medical purposes or for calibration of analytical equipment for example.

Original article was written by Mr. Bryen Smith (Tamaki College) in association with Mr. H. Garrett (N.Z.I.G.) with considerable editing by John Packer. It has been revised for this edition by Heather Wansbrough, John Packer and John Cummings (BOC Gases, formally N.Z.I.G.), following visits to the Glenbrook plant (hosted by John Cummings) and Penrose plant (hosted by Mr. Kevin Benson).