THE PROCESSING OF NATURAL GAS AT KAPUNI

Natural gas in New Zealand is extracted from the ground as a mixture of different hydrocarbons, some gaseous, some liquid. To convert this into a useable product requires the initial separation of the mixture into gaseous and liquid components, and then the purifying and separation of the gaseous component - a process that consists of several steps.

Step 1 - Removal of CO_2 and H_2S
These are both removed from the gas stream using the same reagent: potassium carbonate. This reacts with CO_2 as follows:

$$K_2CO_3 \quad + \quad CO_2 \quad + \quad H_2O \overset{121^{\circ}C}{\leftrightarrows} 2KHCO_3$$

The H_2S is removed using the same reagent, because of the existence of the following equilibrium:

$$K_2CO_3 \quad + \quad H_2S \leftrightarrows KHS \quad + \quad KHCO_3$$

Step 2 - Carbonate regeneration
The potassium bicarbonate solution is then depressurised, making the carbon dioxide less soluble and so causing it to escape from solution. This drives the above equilibrium to the left, and all the carbon dioxide is lost from solution. This is then released into the atmosphere, and the potassium carbonate solution reused.

Step 3 - Removal of water
The gas is cooled, causing much of the water to condense out What remains is absorbed into a solution of triethylene glycol.

Step 4 - Removal of heavier hydrocarbons and fractionation
The dry gas is chilled, causing the heavier hydrocarbons to condense. The liquid and gas are separated and the gas compressed ready for sale as natural gas. The liquid hydrocarbons are separated by a series of distillation columns into four fractions: ethane and lighter, followed by propane, butane and then pentanes and heavier. The lightest fraction is combined with the 'natural gas', the propane and butane are either sold separately or as a mixture (LPG) and the heaviest fraction, so-called "natural gasoline", is combined with condensate from the field and further processed at the Marsden Point refinery.

INTRODUCTION

Natural gas and liquid petroleum gas (LPG) are important fuels used in New Zealand by many homeowners for heating and cooking, as well as in vehicle fuels, gas barbecues etc. Various useful 'petrochemicals' such as ammonia and methanol are also produced as by-products of the natural gas process. The Kapuni field, one of several fields producing gas and LPG in New Zealand, consists of an extensive reservoir of gas and condensate situated 3500-4000m underground. The gas and condensate is recovered from several well sites and piped to a central facility of the Natural Gas Corporation of New Zealand (NGC) which then processes them to produce various commercial end products.

Kapuni gas is a lean natural gas, nearly half of which is non-combustible, about 43% being carbon dioxide. Its composition is given in **Table 1**. The gas also contains 5 mg m^{-3} H_2S, has a calorific value of 27.3 MJ m^{-3} and a specific gravity of 1.07.

The combustible compounds are methane, ethane, propane, butane and other heavier hydrocarbons.

Table 1 - Composition of Kapuni gas before further processing by NGC

Component gas	molar percentage
Carbon dioxide	42.6
Nitrogen	0.3
Methane	45.8
Ethane	5.5
Propane	3.5
Butanes	1.6
Pentanes	0.4
Hexanes and heavier	0.3

*The combined gas from the low temperature and low pressure separators and the stabiliser gas. This is labelled 'sales gas' in **Figure 1** below.

EXTRACTION AND INITIAL PROCESSING

The well sites and initial processing facilities are operated by Shell Todd Oil Services Ltd (STOS). At the well sites the gas and condensate are separated and piped to the STOS Production Station where the condensate is stabilised for pumping to Port Taranaki and subsequent shipment to Marsden Point for refining (see article). The well stream gas is combined with the condensate off-gases and sold for further processing. This initial process is outlined in **Figure 1**.

The hydrocarbons extracted from the ground consist of a complex mixture which can change from gas to liquid to near solid, depending on temperature and pressure. High temperature and low pressure favour the gaseous state. As the mixture of hydrocarbons rises from the reservoir to the well-head on the surface, both temperature and pressure drop so that the discharge from the Kapuni wells is part liquid and part gas. Under normal conditions this mixture arrives at the surface at a pressure between 60 and 120 barg[1] and at a temperature of approximately 65°C. Separation of the well stream into liquid and gas is carried out in several stages, the first being in separators where the pressure is reduced by up to 70 bar.

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[1] The unit 'barg' is a measure of the difference in pressure between the outside atmosphere and the pressure within the vessel containig the gas. 60 barg means that the pressure in the vessels is 60 bar above atmospheric (1 bar = 10^5 Pa), thus if atmospheric pressure is 101.3 kPa, then the pressure within the vessel is 6101.3 kPa or 61 bar.

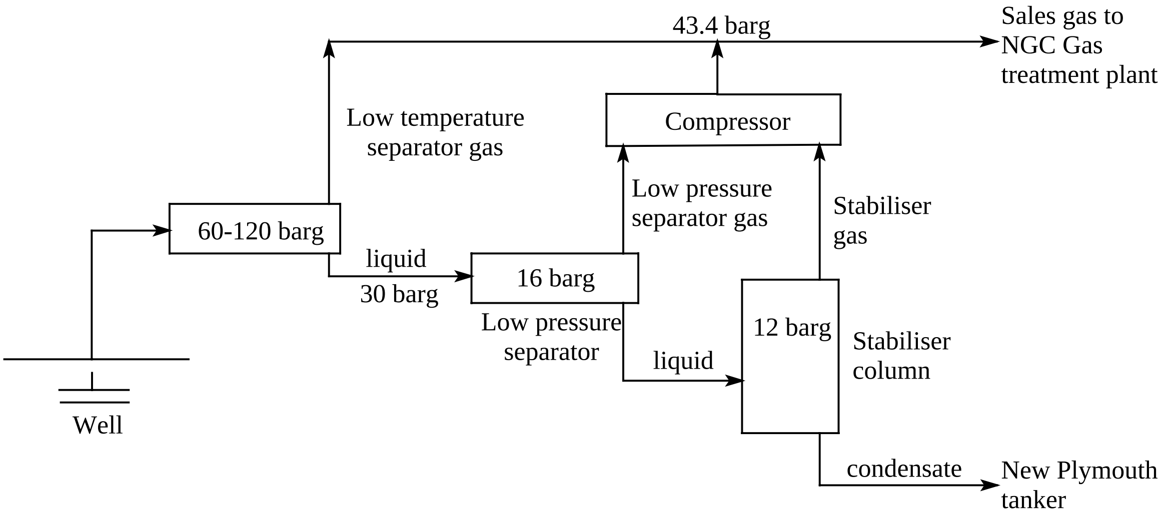


Figure 1 - The extraction and initial processing of natural gas

The first stream of gas, called Low Temperature Separator Gas, is drawn off either for further processing or compressed up to 250 barg and reinjected back into the reservoir. The pressure of the remaining liquid fraction is then further reduced to 16 barg with the production of more gas, Low Pressure Separator Gas (LPS), which is also drawn off for further processing. The residue is condensate and water. The condensate still contains much dissolved gas and this is removed by a distillation column so that the condensate is stabilised before it leaves for the Marsden Point Refinery. This final gas, called stabiliser gas, is mixed with LPS gas and compressed to sales gas pressure (43.5 barg) and combined with the LTS gas. The combined stream is then piped to Natural Gas Corporation's Gas Treatment Plant for further processing.

TREATMENT OF THE GAS STREAM

Step 1 - Removal of CO_2 and H_2S

The non-combustible carbon dioxide must be removed before the gas is suitable for domestic use, and this is done at the treatment plant (**Figure 2**) where the untreated gas is fed into carbon dioxide absorber towers at 43 barg. Here it passes up the towers against a flow of hot potassium carbonate which absorbs the carbon dioxide to give bicarbonate:

$$K_2CO_3 + CO_2 + H_2O \overset{121^{o}C}{\leftrightarrows} 2KHCO_3$$

Potassium carbonate is used because potassium bicarbonate is more soluble than sodium bicarbonate. The incoming gases are hot and under high pressure, which means higher concentrations of salts are attained. The reaction is exothermic and thus absorption of CO_2 is not enhanced by the high temperatures (i.e. the equilibrium constant decreases with increasing temperature), but because the partial pressure of CO_2 is so high, a high level of absorption is in fact achieved. Diethanolamine is added to the potassium carbonate solution to aid the transfer of the CO_2 from the feed gas into the potassium carbonate solution. The increased concentration of dissolved CO_2 pushes the above reaction to the right.

Hydrogen sulphide is also removed in the above process because of a similar acid-base equilibrium reaction involving H_2S:

$$K_2CO_3 + H_2S \leftrightarrows KHS + KHCO_3$$

The H_2S is vented off with the CO_2.

The natural gas, freed of its carbon dioxide, leaves the absorber tower for further treatment which is necessary to remove water and heavier hydrocarbons. These components must be removed because water and hydrocarbons combined at low temperatures can form a solid mixture of hydrates (clathrates) which could completely block the pipeline.

Step 2 - Carbonate regeneration

The potassium carbonate solution is regenerated after use, so that it can be reused and the CO_2 can be vented off. This is done by cycling back the potassium bicarbonate solution at high temperature through a flash column where a sudden drop of pressure to 8 barg drives out most of the gaseous hydrocarbons that have been absorbed in the solution. Then it is fed to the top of the regenerator tower where another pressure drop occurs as it enters. The potassium bicarbonate solution then passes down the tower against a flow of steam. At the lower pressure CO_2 comes off and the equilibrium is driven to the left. The carbon dioxide is vented off at the top of the regenerator tower with steam and the regenerated potassium carbonate which is cycled back to the absorber tower.

$$K_2CO_3 + CO_2 + H_2O \leftrightarrows 2KHCO_3$$

Step 3 - Removal of water

To remove water from the gas, it is first cooled and passed to the gas separator, where much of the water picked up during its passage through the absorber tower is removed through condensation. The gas passes on through the glycol absorber column, where more water is removed from the gas by being absorbed into triethylene glycol ($HOCH_2CH_2OCH_2CH_2OCH_2\text{-}CH_2OH$). The water-saturated glycol is regenerated by heating and recycled through the column.

Step 4 - Removal of heavier hydrocarbons and fractionation

Once the water has been removed, some heavier hydrocarbons are extracted from the gas both to produce LPG (which is more valuable) and to prevent condensation and its associated problems in the distribution system. The gas passes through a final system of heat exchangers and chillers until the heavier hydrocarbons are condensed and recovered as a liquid. This liquid is introduced to a de-ethaniser where ethane and lighter components are stripped out and returned to the product gas stream. The liquid is then fractionated in two further distillation columns to produce commercial propane, commercial butane and natural gasoline (pentanes and heavier). The propane and butane streams can be mixed as required to produce automotive LPG (60:40 propane:butane on a molar basis). The final product gas stream is compressed to 86 barg and then reticulated throughout the North Island *via.* a network of pipelines.

The end products thus consist of propane, butane, LPG, natural gasoline (the liquids) and natural gas (the gas).

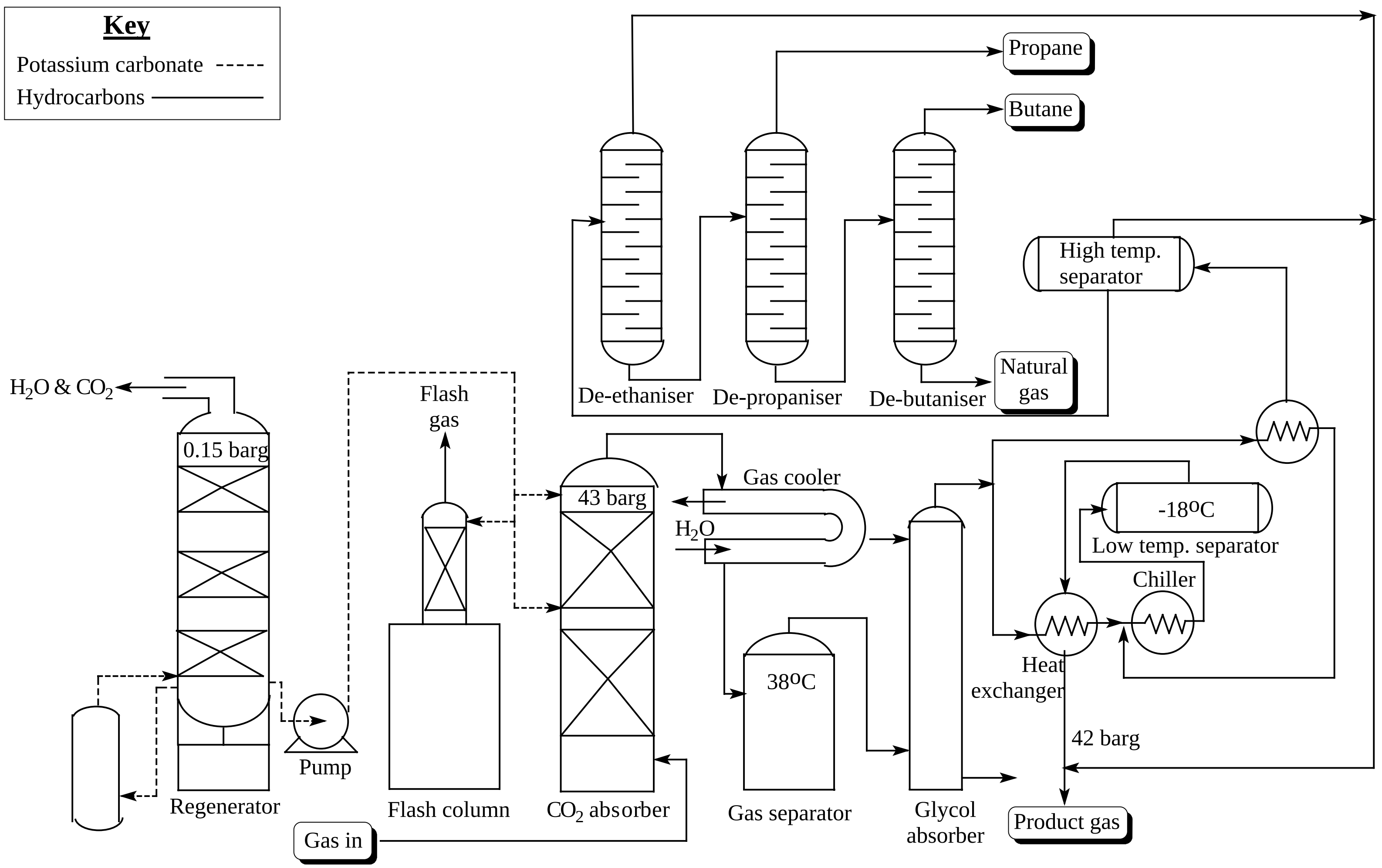


Figure 2 - Flow diagram of the gas treatment plant

THE ROLE OF THE LABORATORY

The primary role of the laboratory is quality control. The analyses that it carries out, to ensure that a high quality product is produced, are outlined below.

Analysis of mixed carbonate and bicarbonate

A plot of pH against the volume of a dilute solution of a strong acid for the titration of a carbonate shows two sharp drops in pH corresponding to the end points of the following reactions:

$$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq)$$
$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2O + CO_2$$

The pH of the first end point is 8.1 and that of the second is 3.8. These end points may be detected with phenolphthalein (pink to colourless) and bromocresol green (blue to yellow) respectively, or by using a pH meter. The volume of acid to the first end point is equivalent to the carbonate content, and the difference between this and the volume between the first and second end points is equivalent to the bicarbonate content. The proportion of carbonate present indicates the effectiveness of the solution regeneration (**Step 2**).

Sulfide

The sulfide (S^{2-}) concentration in solution is determined by precipitating it as zinc sulfide (ZnS) which is then treated with known excess iodate ion (IO_3^-) which oxidises the sulfide to sulfate:

$$4IO_3^- + 3ZnS \rightarrow 4I^- + 3Zn^{2+} + 3SO_4^{2-}$$

The loss of iodate is determined by treating the resultant solution with excess potassium iodide to produce free iodine which is measure by titrating against a standard solution of thiosulfate.

$$6H^+ + IO_3^- + 5I^- \rightarrow 3I_2 + 3H_2O$$
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Diethanolamine (DEA)

The DEA concentration of the solution is determined colorimetrically by reaction with insoluble basic cupric carbonate at pH 14. By using an excess of the insoluble basic cupric carbonate, a blue solution is formed having a colour intensity proportional to the concentration of the alkanolamine in solution. Although mono or triethanolaminesm (MEA or TEA) can be detected, DEA absorbs more strongly than either of these. The reaction is carried out at pH 14, where the colour is most intense, to achieve maximum sensitivity. The DEA is necessary to increase the amount of CO_2 absorbed by the potassium carbonate, so it is important to monitor the amount of DEA present to maximise efficiency.

Iron / Corrosion

Corrosion can be a serious problem in the treatment plant if it is not closely controlled. Hence one of the most important tests the laboratory carries out is to measures the iron content in the carbonate solution to determine the effectiveness of the corrosion inhibitor. The mechanisms of corrosion and its inhibition are complex, the following being a great simplification.

In the absence of an inhibitor the following reactions can occur:

$$Fe + 2CO_2 + 2H_2O \rightarrow Fe(HCO_3)_2 + H_2$$

$$Fe(HCO_3)_2 \rightarrow FeCO_3 + CO_2 + H_2O$$

(the latter reaction only occurs at high temperatures)

Both ferrous bicarbonate and carbonate form non-protective and porous scales on mild steel. In the presence of sodium metavanadate, which is used as a corrosion inhibitor, a protective film of adherent magnetite (Fe_3O_4) is formed:

$$3Fe + 8VO_3^- + 24H^+ \rightarrow Fe_3O_4 + 8VO^{2+} + 12H_2O$$

Above 100°C iron reacts directly with water:

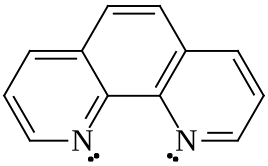
$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

and the hydrogen would tend to reduce any non-protective Fe_2O_3 to Fe_3O_4

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$$

Protective films are likely to suffer erosion from the movement of solutions, and the plant is designed for low solution velocities to preserve the passive protecting film.

The laboratory measures the amount of iron present in the carbonate solution (using a colorimetric method[2]) to determine how well the corrosion inhibitors are functioning. The iron is present as Fe(III) and is reduced by hydroxylamine (NH_2OH) to Fe^{2+} which is treated with a solution of phenanthroline giving an orange red complex which absorbs light at a wavelength of 510nm.



Phenanthroline

Written by C.A. Clancey (Hawera High School) in association with J.S. Hungerford and J. Child (Natural Gas Corporation of New Zealand). Updated by Tony van Gameren (Natural Gas Corporation) with editing by Heather Wansbrough.

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[2] Finding out the concentration of one component of a solution based on the intensity of a colour either caused by the component directly or, as in this case, by a compound containing that component.