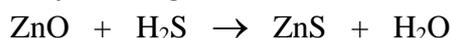


AMMONIA AND UREA PRODUCTION

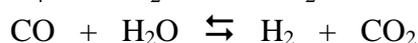
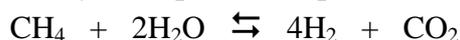
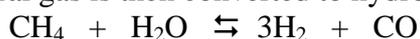
Urea (NH_2CONH_2) is of great importance to the agriculture industry as a nitrogen-rich fertiliser. In Kapuni, Petrochem manufacture ammonia and then convert the majority of it into urea. The remainder is sold for industrial use.

Ammonia synthesis

Ammonia is synthesised from hydrogen (from natural gas) and nitrogen (from the air). Natural gas contains some sulfurous compounds which damage the catalysts used in this process. These are removed by reacting them with zinc oxide, e.g.

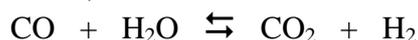


The methane from the natural gas is then converted to hydrogen:



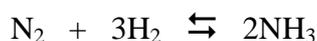
Air is mixed in with the gas stream to give a hydrogen:nitrogen ratio of 3:1.

Water, carbon monoxide and carbon dioxide (all of which poison the iron catalyst used in the ammonia synthesis) are removed. The carbon monoxide is converted to carbon dioxide for use in urea production, and the carbon dioxide removed:



The remaining traces of CO and CO₂ are converted to methane and then the gases cooled until the water becomes liquid and can be easily removed.

The nitrogen and hydrogen are then reacted at high temperature and pressure using an iron catalyst to form ammonia:



Urea synthesis

Urea is made from ammonia and carbon dioxide. The ammonia and carbon dioxide are fed into the reactor at high pressure and temperature, and the urea is formed in a two step reaction



The urea contains unreacted NH₃ and CO₂ and ammonium carbamate. As the pressure is reduced and heat applied the NH₂COONH₄ decomposes to NH₃ and CO₂. The ammonia and carbon dioxide are recycled.

The urea solution is then concentrated to give 99.6% w/w molten urea, and granulated for use as fertiliser and chemical feedstock.

INTRODUCTION

Ammonia and urea are two chemicals which are very important to the New Zealand economy. This article covers a process used by Petrochem in Kapuni, South Taranaki, to synthesise ammonia from natural gas and air, then synthesise urea from this ammonia and carbon dioxide. Annually 105 000 tonnes of pure ammonia (300 T day⁻¹) are produced in

Kapuni, and most of this is converted to urea. Currently 182 000 tonnes of granular urea are produced annually (530 T day^{-1}), but this is soon expected to increase to 274 000 tonnes.

Uses of ammonia and urea

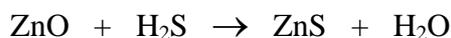
As has been stated above, most of the ammonia is used on site in the production of urea. The remainder is sold domestically for use in industrial refrigeration systems and other applications that require anhydrous ammonia. The urea is used as a nitrogen-rich fertiliser, and as such is of great importance in agriculture, one of New Zealand's major industries. It is also used as a component in the manufacture of resins for timber processing and in yeast manufacture.

THE AMMONIA MANUFACTURING PROCESS

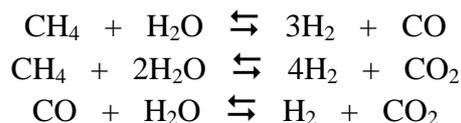
Ammonia is produced in a process known as the Haber process, in which nitrogen and hydrogen react in the presence of an iron catalyst to form ammonia. The hydrogen is formed by reacting natural gas and steam at high temperatures and the nitrogen is supplied from the air¹. Other gases (such as water and carbon dioxide) are removed from the gas stream and the nitrogen and hydrogen passed over an iron catalyst at high temperature and pressure to form the ammonia. The process is shown schematically in **Figure 1**.

Step 1 - Hydrogen production

Hydrogen is produced by the reaction of methane with water. However, before this can be carried out, all sulfurous compounds must be removed from the natural gas to prevent catalyst poisoning. These are removed by heating the gas to 400°C and reacting it with zinc oxide:



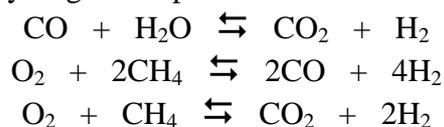
Following this, the gas is sent to the primary reformer for steam reforming, where super-heated steam is fed into the reformer with the methane. The gas mixture heated with natural gas and purge gas to 770°C in the presence of a nickel catalyst. At this temperature the following equilibrium reactions are driven to the right, converting the methane to hydrogen, carbon dioxide and small quantities of carbon monoxide:



This gaseous mixture is known as synthesis gas.

Step 2 - Nitrogen addition

The synthesis gas is cooled slightly to 735°C . It then flows to the secondary reformer where it is mixed with a calculated amount of air. The highly exothermic reaction between oxygen and methane produces more hydrogen. Important reactions are:



¹Air is approximately 78% nitrogen, 21% oxygen and 1% argon with traces of other gases.

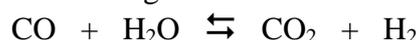


In addition, the necessary nitrogen is added in the secondary reformer.

As the catalyst that is used to form the ammonia is pure iron, water, carbon dioxide and carbon monoxide must be removed from the gas stream to prevent oxidation of the iron. This is carried out in the next three steps.

Step 3 - Removal of carbon monoxide

Here the carbon monoxide is converted to carbon dioxide (which is used later in the synthesis of urea) in a reaction known as the water gas shift reaction:



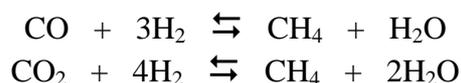
This is achieved in two steps. Firstly, the gas stream is passed over a Cr/Fe₃O₄ catalyst at 360°C and then over a Cu/ZnO/Cr catalyst at 210°C. The same reaction occurs in both steps, but using the two steps maximises conversion.

Step 4 - Water removal

The gas mixture is further cooled to 40°C, at which temperature the water condenses out and is removed.

Step 5 - Removal of carbon oxides

The gases are then pumped up through a counter-current of UCARSOL™ solution (an MDEA solution, see article). Carbon dioxide is highly soluble in UCARSOL, and more than 99.9% of the CO₂ in the mixture dissolves in it. The remaining CO₂ (as well as any CO that was not converted to CO₂ in **Step 3**) is converted to methane (methanation) using a Ni/Al₂O₃ catalyst at 325°C:²



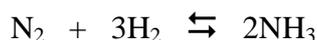
The water which is produced in these reactions is removed by condensation at 40°C as above. The carbon dioxide is stripped from the UCARSOL and used in urea manufacture. The UCARSOL is cooled and reused for carbon dioxide removal.

Step 6 - Synthesis of ammonia

The gas mixture is now cooled, compressed and fed into the ammonia synthesis loop (see **Figure 1**). A mixture of ammonia and unreacted gases which have already been around the loop are mixed with the incoming gas stream and cooled to 5°C. The ammonia present is removed and the unreacted gases heated to 400°C at a pressure of 330 barg and passed over an iron catalyst. Under these conditions 26% of the hydrogen and nitrogen are converted to ammonia. The outlet gas from the ammonia converter is cooled from 220°C to 30°C. This cooling process condenses more the half the ammonia, which is then separated out. The

²These reactions are the reverse of the primary reformer reactions seen in **Step 1**. The catalyst in both cases is nickel, illustrating the fact that a catalyst accelerates both the forward and back reactions of an equilibrium system. At reforming temperatures (~850°C) the methane is almost completely converted to carbon oxides and hydrogen as the reaction is endothermic and favoured by the high temperature. However, at the much lower temperature used for methanation (~325°C), the equilibrium lies to the right and practically complete conversion of the carbon oxides to methane is obtained.

remaining gas is mixed with more cooled, compressed incoming gas. The reaction occurring in the ammonia converter is:



The ammonia is rapidly decompressed to 24 barg. At this pressure, impurities such as methane and hydrogen become gases. The gas mixture above the liquid ammonia (which also contains significant levels of ammonia) is removed and sent to the ammonia recovery unit. This is an absorber-stripper system using water as solvent. The remaining gas (purge gas) is used as fuel for the heating of the primary reformer. The pure ammonia remaining is mixed with the pure ammonia from the initial condensation above and is ready for use in urea production, for storage or for direct sale. Ammonia product specifications are given in **Table 2**.

Table 1 - Composition of the gas stream after each process step[†]

	Feed gas	Step 1	Step 2	Step 3 [*]	Step 5	Ideal
N₂	2.9 [‡]	0.8	21.7	19.9	24.7	25
H₂	—	68.3	56.5	60.1	74	75
CO	—	6.2	8.9	0.1	—	—
CO₂	4.1	14.5	11.8	18.9	—	—
CH₄	83.4	10.2	0.7	0.7	1.0	—
Ar	—	—	0.3	0.3	0.3	—
other hydrocarbons	9.6	—	—	—	—	—

[†]Water is not listed among the gases considered because its levels are highly variable. All water is eliminated after step 4.

[‡]All figures are given in mol % (i.e. the percentage of the total number of moles of gas present that are due to this gas).

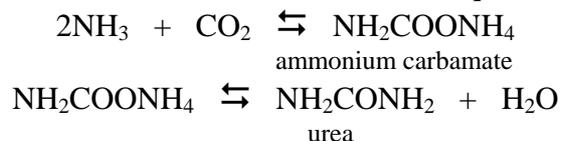
^{*}The gaseous composition after **Step 4** is the same as that after **Step 3** as **Step 4** is simply the removal of water.

Table 2 - Ammonia specifications

Component	Composition
Ammonia	98 % minimum
Moisture	1500 g T ⁻¹ maximum
Oil	85 g T ⁻¹ maximum
Iron	1.0 g T ⁻¹ maximum

THE UREA MANUFACTURING PROCESS

Urea is produced from ammonia and carbon dioxide in two equilibrium reactions:



The urea manufacturing process, shown schematically in **Figure 2**, is designed to maximise these reactions while inhibiting biuret formation:



This reaction is undesirable, not only because it lowers the yield of urea, but because biuret burns the leaves of plants. This means that urea which contains high levels of biuret is unsuitable for use as a fertiliser. The structure of these compounds is shown in **Figure 3**.

Step 1 - Synthesis

A mixture of compressed CO₂ and ammonia at 240 barg is reacted to form ammonium carbamate. This is an exothermic reaction, and heat is recovered by a boiler which produces steam. The first reactor achieves 78% conversion of the carbon dioxide to urea and the liquid is then purified. The second reactor receives the gas from the first reactor and recycle solution.

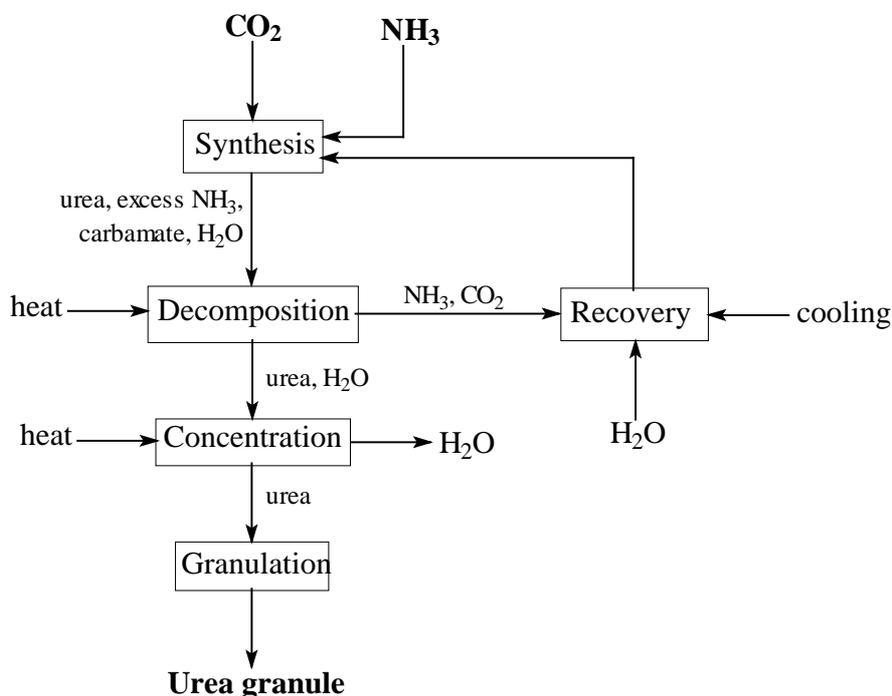


Figure 2 – Schematic representation of urea synthesis

from the decomposition and concentration sections. Conversion of carbon dioxide to urea is approximately 60% at a pressure of 50 barg. The solution is then purified in the same process as was used for the liquid from the first reactor.

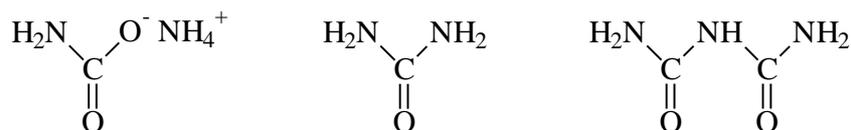


Figure 3 - Some chemicals of interest in urea production

Step 2 - Purification

The major impurities in the mixture at this stage are water from the urea production reaction and unconsumed reactants (ammonia, carbon dioxide and ammonium carbamate). The unconsumed reactants are removed in three stages³. Firstly, the pressure is reduced from 240 to 17 barg and the solution is heated, which causes the ammonium carbamate to decompose to ammonia and carbon dioxide:



At the same time, some of the ammonia and carbon dioxide flash off. The pressure is then reduced to 2.0 barg and finally to -0.35 barg, with more ammonia and carbon dioxide being lost at each stage. By the time the mixture is at -0.35 barg a solution of urea dissolved in water and free of other impurities remains.

At each stage the unconsumed reactants are absorbed into a water solution which is recycled to the secondary reactor. The excess ammonia is purified and used as feedstock to the primary reactor.

Step 3 - Concentration

75% of the urea solution is heated under vacuum, which evaporates off some of the water, increasing the urea concentration from 68% w/w to 80% w/w. At this stage some urea crystals also form. The solution is then heated from 80 to 110°C to redissolve these crystals prior to evaporation. In the evaporation stage molten urea (99% w/w) is produced at 140°C. The remaining 25% of the 68% w/w urea solution is processed under vacuum at 135°C in a two series evaporator-separator arrangement.

Step 4 - Granulation

Urea is sold for fertiliser as 2 - 4 mm diameter granules. These granules are formed by spraying molten urea onto seed granules which are supported on a bed of air. This occurs in a granulator which receives the seed granules at one end and discharges enlarged granules at the other as molten urea is sprayed through nozzles. Dry, cool granules are classified using screens. Oversized granules are crushed and combined with undersized ones for use as seed. All dust and air from the granulator is removed by a fan into a dust scrubber, which removes the urea with a water solution then discharges the air to the atmosphere. The final product is cooled in air, weighed and conveyed to bulk storage ready for sale.

³This three step process is used to discourage two undesirable reactions — urea hydrolysis:



and biuret formation:

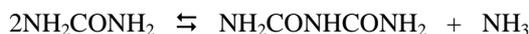


Table 3 - Urea granule specifications

Component	Concentration
Nitrogen	46 % minimum by weight
Biuret	1.0 % maximum by weight
Moisture content	0.3 % maximum by weight
Sizing	90% 2 - 4 mm by weight

UTILITIES

The ammonia and urea manufacturing facilities are separate, so each has its own utilities. These are listed below.

Ammonia manufacture

Heat recovery

The heat of the gas from the primary reformer (**Step 1**) is used to produce steam for the primary reformer using a boiler. The gas is then discharged. Heat from the process gas from the secondary reformer (**Step 2**) is used to produce steam for a turbogenerator.

Water recycling

Excess water from the water gas shift converter, the methanator and the ammonia synthesis loop is used for boiler feed water and as the absorbing water for ammonia recovery.

Carbon dioxide stripper

The used UCARSOL is sent to the carbon dioxide stripper. Here the UCARSOL is heated to remove a mixture of CO₂ and water, cooled and reused. The water is removed from the CO₂ by condensation and the pure CO₂ sent directly to the urea plant for compression and use in urea synthesis.

Ammonia recovery

Gases purged from the ammonia synthesis loop and gases collected during ammonia decompression are mixed and sent to the ammonia recovery system. Here the gas mixture is introduced at the bottom of a column and passes up through a counter-current of cold water. 96% of the ammonia in the gas is absorbed into the water, leaving a gas mixture that is used as a fuel gas to heat the primary reformer. The ammonia is distilled out of the ammonia-water mixture, condensed and pumped to join the rest of the ammonia from the ammonia synthesiser.

Urea manufacture

Heat recovery

The heat of the reaction in which ammonium carbamate produces steam at 7 barg. This is used in the decomposition and evaporation sections for heating.

Ammonia and carbon dioxide recovery

During urea decomposition a mixture of gaseous carbon dioxide and ammonia is collected and absorbed into a dilute aqueous urea solution. This mixture is recycled by being fed back

into the secondary urea reactor. The excess ammonia is condensed and used as feedstock to the primary reactor.

Water recycling

Evaporated water from the concentration step is used during the third stage of decomposition as the initial recycle solution.

THE ROLE OF THE LABORATORY

Ammonia production

- The laboratory monitors the gaseous mixture exiting each vessel at each stage in the process using gas chromatography. The concentration of each component during the process is kept at a precalculated design figure and laboratory results are compared to these figures. Adjustments are made to the process based on the laboratory results to bring the process back to the design figures.
- The UCARSOL solution is analysed daily to determine the solution strength. The solution strength must be kept within a defined range and additions to the system are made according to laboratory results.
- Liquid ammonia product is analysed to ensure that impurity concentrations are below maximum levels set.

Urea Production

- The laboratory carries out analysis at various stages of granulation for size distribution. The process is adjusted accordingly to meet final product size specifications.
- The final product is analysed for moisture, biuret, formaldehyde and pH as a check on the process and to ensure customer specifications are met.

In addition, boiler and cooling waters are analysed to ensure that their composition is such that corrosion is minimised.

Trouble shooting is often required to source biuret or excessive moisture during intermediate stages of the urea process.

ENVIRONMENTAL IMPLICATIONS

The ammonia and urea complex is operated in accordance with stringent safety and environmental standards. The Petrochem complex produces effluent in the form of storm water and waste water from the manufacturing process. All effluent is directed to large holding ponds where it is treated and carefully checked as to its composition prior to discharge. The effluent is spray irrigated onto Petrochem's pastures surrounding the complex. Many waste minimisation measures are carried out during the process, resulting in the plant having little effect on the environment.

FINANCIAL CONSIDERATIONS

The process uses three main raw materials: natural gas, air and water. Petrochem's plant is situated adjacent to the Kapuni gas treatment plant so natural gas is readily accessible. Natural gas is used for both fuel gas and as a source of carbon dioxide and hydrogen for the process. Air is, of course, in abundant supply. Water is pumped from the nearby Waingongoro stream for head water to the boilers, cooling water and process water. This water is treated after exiting the process and returned to the stream. Thus all raw materials are cheap and readily available.

Costs are minimised throughout the process by using waste heat boilers and heat exchangers. There is a co-generation plant and turbogenerator on site which together produce around 80% of the power needed to run the plant.

Petrochem has undergone an upgrade to increase the production capacity of the plant. When this expansion is fully commissioned, production capacity will increase to 750 tonnes of urea per day.

Article written by J. C. Coplestone (Petrochem) and Dr. C. M. Kirk (Taranaki Polytechnic) with revisions by S. L. Death, N. G. Betteridge and S. M. Fellows (all of Petrochem) and editing by Heather Wansbrough.