1,620 Metric Tons/Day
Ammonia Plant
Introduction
Designed by M.W. Kellogg, the Ammonia Plant was commissioned in 1980 and shut down in October 2002. The plant had an original capacity of 1,350 metric tons per day but has been upgraded to its current capacity of 1,620 metric tons per day.

Raw Materials
The Ammonia Plant Process is operated using basic raw materials of Natural Gas, Water and Air. The different reactions in the process require specific catalysts.
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Catalysts, composition, weight in vessel and time before replacement

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### AMMONIA PLANT CATALYSTS

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition</th>
<th>Weight</th>
<th>Life (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogenator</td>
<td>Co, Mo, Al</td>
<td>10 Tons</td>
<td>9 Years*</td>
</tr>
<tr>
<td>Desulphurizer</td>
<td>Zn O</td>
<td>64 Tons</td>
<td>9 Years*</td>
</tr>
<tr>
<td>Primary Reformer</td>
<td>NiO2</td>
<td>22 Tons</td>
<td>3 Years</td>
</tr>
<tr>
<td>Secondary Reformer</td>
<td>NiO2</td>
<td>40 Tons</td>
<td>8 Years</td>
</tr>
<tr>
<td>High Temp. Shift</td>
<td>Fe, Cr</td>
<td>45 Tons</td>
<td>8 Years</td>
</tr>
<tr>
<td>Low Temp. Shift</td>
<td>Cu, Zn, Al</td>
<td>66 Tons</td>
<td>3 Years</td>
</tr>
<tr>
<td>Methanator</td>
<td>NiO2</td>
<td>43 Tons</td>
<td>8 Years</td>
</tr>
<tr>
<td>Ammonia Synthesis</td>
<td>Fe</td>
<td>203 Tons</td>
<td>8 Years</td>
</tr>
</tbody>
</table>
Natural Gas

Natural Gas is Methane, and used as a fuel in the furnace for heating the exterior of the primary reformer tubes. It’s used as process material inside the primary reformer tubes for the production of Hydrogen. It’s delivered to site by pipeline at 25bar. It must be pressurized to over 40 bar to run the process.

Fresh Water

Potable Water is delivered to site by pipeline from a local authority. It must be de-mineralized before conversion to steam. It is used in the primary reformer as steam with natural gas where they both react to form hydrogen and carbon oxides. Correct treatment of the water is critical for the continuous operation of the plant.
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Fresh water storage 15,000m³. Demineralized water storage 500m³
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Water Treatment
The water treatment plant (2008L), water is de-mineralized using as a first step, one of three parallel cationic streams. This is followed by a common de-gasser to remove carbon dioxide and then by one of three parallel anionic streams and finally on to one of two mixed bed streams again in parallel. The cationic and anionic units are regenerated each shift and the mixed beds are regenerated weekly depending on the sodium and silica slippage from the cation and anion exchangers respectively.

Condensate Reuse
The de-mineralization unit treating the process condensate is made up of two cationic resin beds followed by a common de-gasser and one mixed bed. The process condensate is stripped of methanol, excess ammonia and carbon dioxide in the 103E stripper by a heat exchanger at the bottom of 103E and the stripped condensate is cooled before the cationic exchanger inlet. A mixed bed exchanger unit treats surface condensate from the compressors.

(Treatment became optional when the surface condensate coolers were fitted with chloride detectors (conductivity alarms) eliminated the necessity for continuous treatment.)
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ENERGY RECOVERY FROM PROCESS

Demineralised Water 100t/h → Waste Heat Recovery From Ammonia Plant

Waste Heat Recovery
355t/h Steam at 105bar

RECOVERY of CONDENSATE 220t/h

Natural Gas Reforming & Shift Reactions

Condensate Recovery 60t/h

For Start up

355t/h Steam at 105bar → HP TURBINE OF SYNTHESIS COMPRESSOR

11.9 mw

40bar Steam

Waste Heat Recovery

10t/h 40t/h 55t/h 32t/h 73t/h 40t/h

5mw 6.9mw 4mw 9.1mw 5mw

other users

Synthesis Turbine

Process Air Turbine

Refrigeration Turbine

CO2 Turbine

Small Process Turbines

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Sea Water
The main cooling requirements are the fresh tempered cooling water closed system, the surface condenser cooling, Ammonia cooling in the 127°C’s, carbon dioxide to atmosphere in 110°C and Benfield solution cooling. Seawater is pumped at 25,000 t/h from the River Lee Estuary.

Combustion Air
Air is also used for combustion of natural gas in the primary reformer and is supplied to the burners by a forced draught fan.

This is a critical plant area and one can observe the air inlet to the fan and also the second fan that draws the combustion gases from the primary reformer. This induced draught fan is much higher capacity than the forced draught fan so the furnace system always runs under a slight negative pressure. So there is no danger of combustion gases leaking from any part of the heat recovery section as the combustion gases are cooled on route to atmosphere.
Combustion Air continued

The temperature of the combustion gases is 1050°C at the primary-reformer- furnace so heat recovery is an essential part of the process. There are several heat recovery units in this waste heat recovery section of the plant reducing the temperature from 1050°C to 135°C at the discharge point.

This area was one of the significant plant modifications where the Steam Superheater was redesigned to give a better heat transfer efficiency resulting in a lower temperature in the combustion gases to atmosphere.
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Process Air
Air is filtered, compressed to 35bar using a steam turbine powered compressor and fed to the process at the inlet of the secondary reformer.

Production Process
The natural gas is divided into two streams, fuel gas and process gas.
The process gas is the main source of hydrogen and is first pressurized to 42bar using two natural gas compressors.
The natural Gas is odorless when taken from the gas field but must by law be given a distinctive odor. Sulphur compounds such as Methyl, Ethyl and Tertiary-Butyl Mecraptans are added to give the gas a recognizable odor. Sulphur compounds are catalyst poisons in the ammonia plant and the process must remove this sulphur to avoid catalyst damage.
Overview of the Ammonia Plant, Steam System, Compressors, Reaction Vessels and Storage Tanks.
Desulphurization

The Sulphur compounds in the process gas are converted into hydrogen sulphide using hydrogen and a catalyst made up of cobalt & molybdenum oxides. There are 10te of catalyst in the vessel. A hydrogen rich gas stream from the synthesis loop supplies the hydrogen. This is taken from the re-cycle stage of the 103J – Synthesis gas compressor.

The hydrogen sulphide formed is removed by absorption onto zinc oxide forming zinc sulphide and is retained in these two vessels. There are 64te of Zinc Oxide in the two vessels.

Primary Reformer

In the primary reformer steam and natural gas are added in a steam to gas ratio of 3:1. So 100te steam and 33te of natural gas per hour are added to the primary reformer tubes at a pressure of 32bar. Before entering the catalyst filled tubes the mixture is pre-heated to 500°C by the combustion gases leaving the reformer furnace.
Primary Reformer continued

The reforming takes place in 520 tubes filled with promoted nickel oxide catalyst (22te) and the temperature of reaction is 820°C. This reaction is exothermic. Heat is supplied by burning natural gas in 198 burners in the roof of the furnace. There are also 11 burners surrounded by firebricks on the floor of the furnace at the outlet end of the reformer tubes. The process gases and steam flows downward in the catalyst filled tubes. The tubes are divided into ten rows of 52 tubes. 51 of these in each row of tubes are filled with catalyst but one tube in the middle of each row is a riser and does not contain catalyst. This tube has no restriction and is capable of transporting the total flow from the other 51 catalyst filled tubes upwards. The tubes are welded into a common header along the bottom to allow the gases leaving the catalyst filled tubes to run to the empty tube which carries the gases in the opposite direction up to another header meeting the other outlets of other rows. So there are 10 risers taking reformed gases to a common header going on to feed the secondary reformer.
Primary Reformer continued

The gas leaves the primary reformer as a mixture of gases but mostly hydrogen the first of the elements needed for the ammonia synthesis, the approximate composition at this stage is, 70% H2, 10% CO2, 10% CO, and 10% methane.

Approximately 30 te of water and 30te of natural gas is converted to hydrogen and carbon oxides at this stage so more steam must be added. It is important to remember that the preferred reactions in the primary & secondary reformer depend on excess water being present.
Secondary Reformer
The next step is the addition of air and steam. This is pre-heated by waste heat from the combustion gases to 455°C. The air is the source of nitrogen for the ammonia synthesis. The volume of air is designed to give a Hydrogen to Nitrogen ratio of 3:1 (H2:N2) in the gas stream following the removal of carbon oxides, steam and methanol.

This air and steam at 455°C meets the mixture of steam and gas from the primary reformer at 825°C at an inverted burner at the top of the secondary reformer (40te NiO catalyst). The remaining methane is reformed and the temperature increases to 920°C at the exit. This vessel is surrounded by water jackets to keep the metal surface cool.

Approx. composition: 57% H2, 22% N2, 13% CO, 7% CO2, 0.3% CH4.

The gases exit the secondary reformer through two waste heat boilers 101C A&B each producing 100 te steam per hour. The boilers are high heat flux Bayonet/scabbar type boilers. They are followed by a shell and tube boiler 102C 50te/hr capacity. These exchangers utilize the excess heat in the process stream.
Secondary Reformer continued

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100bar Steam 340 °C

Process Air & Steam

455oC

500oC

830oC

101F Steam Drum

101CA/CB

920oC

Water Jackets

Primary Reformer

Secondary Reformer

Fuel

Air

Steam

Natural Gas - Desulphurised

337 °C

208 °C

370 °C

230 °C

103-C

104-C

112-C

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High and Low Temperature Shift Reactions

The temperature of the process gas is now down to 337°C and enters the high temperature shift reactor. The catalyst here is Iron & Chromium oxide, (45te) and the reaction is conversion of carbon monoxide to carbon dioxide using steam and producing Hydrogen, the temperature increasing to 370°C.

The next step, is the low temperature shift reaction and an inlet temperature of 208°C is required. This temperature is achieved using three heat exchangers and by the addition of water to a u-tube where the heat of vaporization causes the reduction in temperature. The 103°C, a shell and tube boiler and produces steam. The 104°C exchanges heat with gases leaving the Benfield absorber. Water is injected into the gas stream as it passes through a u-tube assembly and finally a tempered water exchanger 112°C may be used or bypassed as required to meet the inlet temperature requirements.

The gases leaving the low temperature shift are at 230°C and go on to boil the lean benfield solution at the bottom of the stripper in the 105°C A&B re-boilers.
Carbon Dioxide Removal

At this point the removal of carbon dioxide is one of the key limiting factors in the plant capacity.

Carbon dioxide is removed in the absorber by allowing the gas to flow upwards against a flow of 32% potassium Carbonate solution in a tower containing a packing of metal rings. The carbon dioxide dissolves in the Potassium Carbonate to form Potassium Bicarbonate. The high pressure assists the absorption of the carbon dioxide. The potassium Carbonate contains a mixture of amines, diethanolamine, triethanolamine and LRS10 (A proprietary mixture of amines) to increase the rate that carbon dioxide is absorbed and desorbed.

1-% vanadium is added also to protect the mild steel tower from corrosion. The potassium bicarbonate now rich in Carbon dioxide is then passed to the second tower packed with a similar material and the pressure is reduced to 0.5bar. The carbon dioxide is stripped from the solution again aided by the amine additive and the boiling action in the 105C’s reboilers drive off the remaining carbon dioxide.
The gases then pass through 102F where water is knocked out and returned as process condensate to 103E for steam stripping of methanol and ammonia. The stripped condensate is then passed through a cation exchange resin bed followed by a de-gasser and finally to a mixed bed ion exchanger unit before reuse as boiler feed water. *(The Benfield low heat system was another significant modification improving plant efficiency.)*
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Carbon Dioxide Removal continued
Methanation

The gases leaving the benfield go through knock out pots to remove water before going on to the methanator where the small traces of carbon oxides are converted to methane (Carbon oxides and water are poisons to the iron catalyst in the synthesis converter and must be removed). The catalyst in the methanator is the same material, promoted nickel oxide, as that in the reformer tubes. However, the reaction is the reverse of that in the primary reformer and this is possible because there is no water present in the process stream going through the methanator. The reaction here generates heat when carbon oxides and hydrogen recombine to form methane (Methane is not a poison to the synthesis catalyst). The gases are then cooled by boiler feed water before going on to the first compression stage of the 103J compressor.

Methane builds up in the Synthesis Loop with other inerts introduced from the air through the secondary reformer. They are removed through a Hydrogen Recovery unit where the ammonia is scrubbed with water and sent to the urea plant for reuse. The hydrogen is separated in a set of prisms by diffusion and recycled to make more ammonia. The methane is burned with the fuel gas.
Ammonia Synthesis

The 103J compressor has three compression stages, stage 1, stage 2 and recycle. The process gases in the synthesis loop recirculate in the ammonia rich loop, between the synthesis converter and the 106F (ammonia, knock out vessel). The gasses leaving the 106F now low in ammonia and containing make up gas from the second stage of the 103J return to the synthesis converter via the recycle stage of the 103J.

Ammonia is made up of 3 molecules of hydrogen and 1 molecule of Nitrogen.

Heat is generated by this reaction so low temperature would favor the reaction, however the temperature is maintained high to get a faster generation of a smaller percentage of ammonia followed by rapid removal of over 90% of the ammonia after it is formed.

Once the synthesis reaction is established and the catalyst is fully reduced the gases entering the synthesis converter catalyst contain 1.5-% ammonia the process stream leaving the synthesis converter contains 17% ammonia.
Ammonia Synthesis continued

Because the reaction gives out heat and temperatures above 550°C will damage the catalyst the temperature is controlled between 350°C and 500°C by gas flow through the catalyst bed in the synthesis converter.

The synthesis converter was one of the most significant modifications that improved the efficiency of the plant. The original converter was configured to have a gas flow axially through the vessel. This was modified to give radial flow through the catalyst, which gave a shorter path with lower pressure differential. A smaller particle size catalyst could also be used. This modification increased the ammonia concentration at the outlet of the converter from 14% to 17%.
Ammonia Synthesis continued

Boiler Feed

124C A/B
121C
123C
130C
118C
140C
117C
187bar Pressure
119C
350°C to 530°C
AMMONIA TO 200Tons STORAGE
AT - 33°C

Steam Turbine

N2 + 3H2 → 2 NH3 + HEAT
1 mol + 3 mol → 2 mol

Synthesis converter, heat exchangers, compressor and flow pattern.
The ammonia is sent for storage in two refrigerated tanks each with a capacity of 15,000te. The tanks have a separate refrigeration plant to maintain the temperature at -33°C. The tanks are mild steel and are enclosed in a concrete capsule with a 1 meter gap between the concrete and the tank. There is a pumping system for loading trains and sea going tankers. It is also possible to import ammonia by ship if required.
1,620 MTPD Ammonia Plant - Modifications

- Monsanto hydrogen recovery unit
- Casale modified ammonia converter
- A Benfield low heat unit in the CO2 removal system
- A suction cooler fitted to synthesis gas compressor
- Extra heat recovery coil in the convection section of the primary reformer
- Reformer tubes were replaced in 1996, only in service 5 years. Tube material is paralloy H 39 WM (micro alloy). Header material is paralloy CR 32 W. Number of tubes- 520
- A number of heat exchangers have been recently replaced, including:
  - 116-C, Syn’gas compressor 1st stage aftercooler
  - 129-C, Syn’gas compressor interstage chiller
  - 102-C, secondary waste heat boiler
- New spare exchangers include:
  - 136-C, Methanator feed exchanger
  - 104-C, Methanator feed heater
Spare tube bundles for both waste heat boilers are available.

A new 114-C, Methanator effluent/boiler feed water heater, is partially constructed and available for completion.

Major plant overhauls took place at frequencies that varied between two and four years.

Compressor details- (Spare rotors for these machines):

- Synthesis compressor manufactured by Dresser Clark: twin-case, centrifugal, Models 463B 5/5 & D373bR 8/1, Siemens Turbine Drive.
- Air compressor manufactured by GHH: twin-case, centrifugal, Type Tkd 7/4.4 & Tk 6.5/5.1, Siemens Turbine Drive.
- Refrigeration compressor manufactured by GHH: twin-case, centrifugal, Type Tkz 6/6.4 & Tk 6/5.4, Siemens Turbine Drive.
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Other Equipment-Turbines Covered

Absorber 101-E

Stripper 102-E
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Air Compressor 101-JA
part 1

Ammonia Compressor 1015-J

Synthesis Gas Compressor 103-J
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Secondary Reformer 103-D

Various Equipment

Various Equipment 105 CA/CB
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