Ammonia is generally manufactured from natural gas using the steam reforming process. Other feedstocks and processes are used but these are not described here. There are several reaction stages and catalysts are key to the economic operation of modern ammonia production plants. Diagram 1 illustrates the chemistry of the ammonia process and the basic materials of the catalysts used.

The first stage is purification where impurities, mainly sulphur compounds, are removed from the gas stream.

Steam reforming is performed in two stages. In the primary stage, the endothermic reactions take place at pressures around 30 bar and temperatures of 800°C or higher. This is followed by an exothermic secondary reformer where air is added to the partially reformed gas stream.

The carbon monoxide in the gas leaving the secondary reformer is converted to carbon dioxide in the shift reactors and then removed by scrubbing from the gas stream. Any residual carbon oxides are then converted back to methane by methanation before compression of the hydrogen and nitrogen to ammonia synthesis pressure.

The final reaction stage is ammonia synthesis where the hydrogen and nitrogen combine to form ammonia. This reaction stage takes place at high pressure (100-350 bar) and is highly exothermic.

Diagram 2 shows a simplified block diagram of a typical 1000 tonne/day ammonia plant including details of operating temperatures, catalyst volumes, KATALCO catalyst and gas compositions.

The economics of ammonia production require careful energy management as illustrated by the flowsheet in Diagram 3 which shows many heat exchangers are necessary to optimised heat recovery as well as to generate the steam required for process purposes.
CHEMISTRY OF AMMONIA PROCESS

HYDRODESULPHURISER (Sulphur Removal)

- Natural Gas

- RSH + H₂ → RH + H₂S
- HCl + NaAlO₂ → Al(OH)₃ + NaCl
- H₂S + ZnO → ZnS + H₂O
- Catalyst: CoMo/NiMo, Modified Alumina, Zinc Oxide

PRIMARY REFORMING (Steam Reforming)

- CH₄ + H₂O → 3H₂ + CO
- CO + H₂O → H₂ + CO₂
- Catalyst: Nickel Oxide

SECONDARY REFORMING (Air Addition)

- CH₄ + H₂O → 3H₂ + CO
- 2H₂ + [O₂ + N₂] → 2H₂O + N₂
- Catalyst: Nickel Oxide

HIGH TEMP SHIFT (CO Conversion)

- CO + H₂O → CO₂ + H₂
- Catalyst: Iron/Cr/Cu

AMMONIA SYNTHESIS (Ammonia Formation)

- N₂ + 3H₂ → 2NH₃
- Catalyst: Fused Promoted Magnetite

METHANATOR CO/CO₂ Polishing

- CO + 3H₂ → CH₄ + H₂O
- CO₂ + 4H₂ → CH₄ + 2H₂O
- Catalyst: Nickel Oxide

CO₂ Removal

- K₂CO₃ + H₂O + CO₂ → 2KHCO₃
- 2KHCO₃ → K₂CO₃ + H₂O + CO₂

LOW TEMP SHIFT (CO Conversion)

- CO + H₂O → CO₂ + H₂
- Catalyst: Cu/Zn/Al

Diagram 1
Simplified block diagram of typical 1000 tonne/day ammonia plant

Diagram 2
Simplified flowsheet for typical ammonia plant

Natural Gas

Air

Steam superheater

Steam raising

Cooling

Reboiler

CO₂ Removal

H₂

Hydrodesulphuriser

Primary Reformer

Secondary Reformer

High Temperature Shift

Low Temperature Shift

Heat Recovery

Steam raising

Cooling

Refrigeration

Condensate

Cooling

Quench

Purge Gas

Liquid Ammonia

Ammonia Synthesis

Diagram 3