Annex 3.2 Industrial Processes Sector-ammonia production-Kellog process detailed description

In all the Romania Ammonia Production installations the **Kellogg process** is used. This type of technology is based on steam reforming of methane. There are some aspects related with upgrading the installations and the chemical solutions used to absorb carbon dioxide from synthesis gas of ammonia. All the solutions used in absorption of carbon dioxide contain the potassium carbonate-K_2CO_3. Carbon dioxide is resulted from the regeneration process of the absorption solution.

Typically, carbon dioxide resulting from the production process is used to manufacture of urea. If urea production plant is not functioning, carbon dioxide is released into the atmosphere.

During the production process of ammonia use Kellogg process the raw material used are: methane gas and atmospheric air.

The main steps of technological process are:

- Compression of natural gas;
- Desulphurization of natural gas;
- Primary catalytic reforming of natural gas;
- Secondary catalytic reforming, with air and water vapor;
- Catalytic conversion of carbon monoxide into carbon dioxide, in two steps of temperature;
- Synthesis gas purification (CO_2 removal with K_2CO_3);
- Synthesis gas methanation;
- Ammonia synthesis.

The main product is liquid ammonia.

On industrial scale, ammonia is produced by synthesis from nitrogen and hydrogen. In Romania the raw materials used are:

  - Natural gas as hydrogen source;
  - Air, as nitrogen sources.

From Ammonia Production process results the next main products:

  - Liquid ammonia 99.7% - 99.9%;

- Carbon dioxide CO_2

Liquid ammonia could be used for:

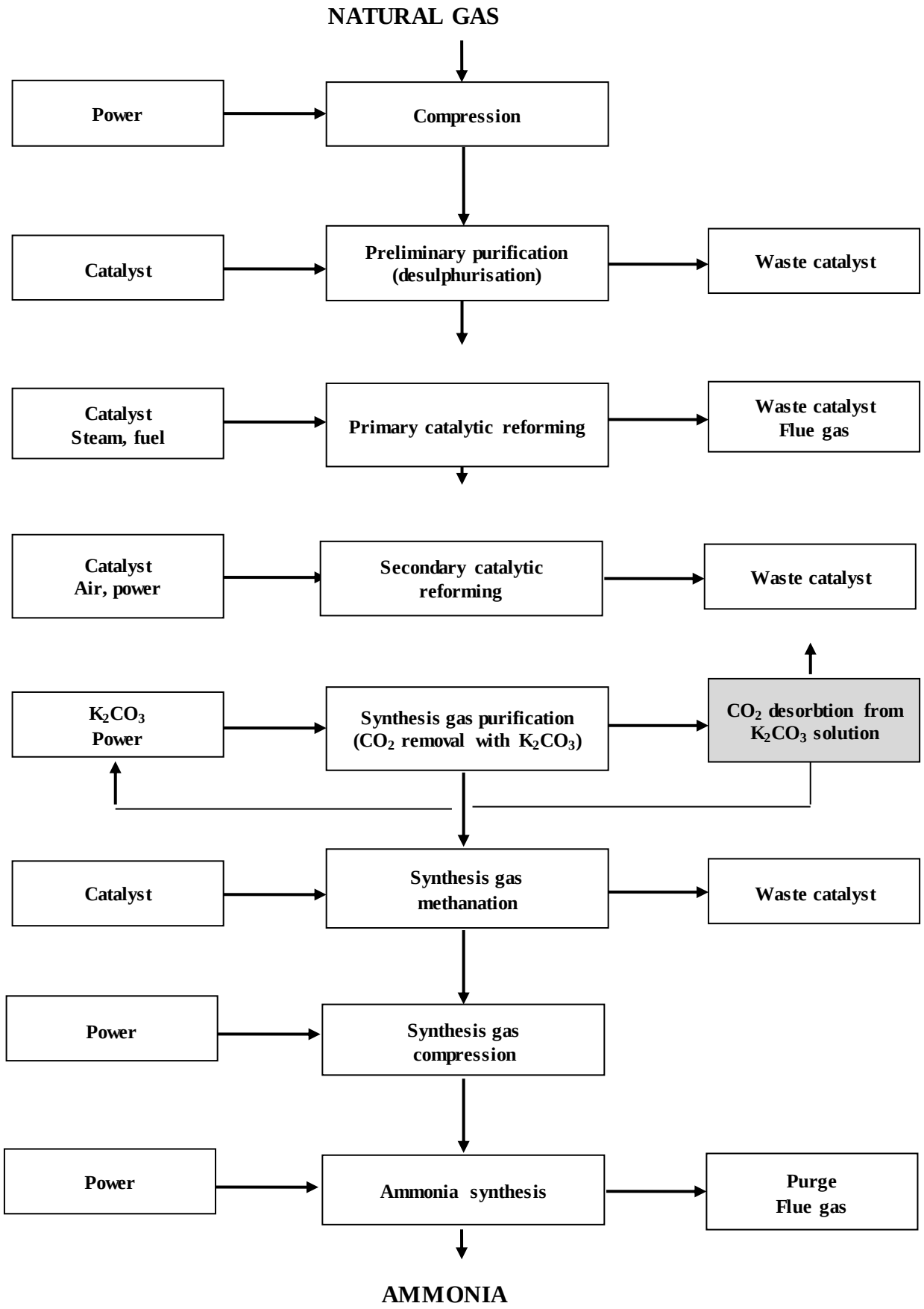
- Urea production;
- Production of ammonium nitrate (NH_4NO_3);
- Production of complex fertilizers.

Carbon dioxide could be used for:

- Urea production;
- Methanol production.

The figure below illustrates the Kellogg diagram flow process of the ammonia obtaining process.

Figure 1 Diagram flow process of the Ammonia obtaining process



Because in all the Ammonia Production facilities Kellogg process is using (process than is based on the steam reforming of methane) main chemical reactions are common to all installations:

Prior purification of natural gas

In the presence of hydrogen and a catalyst with molybdenum, oxygen is converted completely into water and sulfur from organic compounds is related to hydrogen sulfide, according to reactions:

$1/2\ O_2 + H_2 = H_2O$

$R\text{-}SH + H_2 = R\text{-}H + H_2S$

H_2S is detained by ZnO catalyst:

$H_2S + ZnO = ZnS + H_2O$

Catalytic reforming of natural gas

Obtaining the hydrogen to synthesize ammonia takes place in two stages:

- The primary steam reforming on NiO catalyst:

$CH_4 + H_2O = CO + 3\ H_2$

$CO + H_2O = CO_2 + H_2$

- Secondary reforming on NiO catalyst at 950-980 ° C:

$CH_4 + 1/2\ O_2 = CO + H_2$

$CH_4 + O_2 = CO_2 + H_2$

$CO + 1/2O_2 = CO_2$

$2H_2 + O_2 = 2H_2O$

Obtained gas containing 56% H_2, 12% CO, 9% CO_2, 22% N_2 and CH_4 below 0.4%

Purification of carbon dioxide gas resulting in earlier stages

Gas purification is done by washing with hot potassium carbonate solution:

$K_2CO_3 + CO_2 + H_2O = 2\ KHCO_3$

Synthesis gas Methanisation

Residual content of carbon oxides ($CO + CO_2$) is removed by hydrogenation based on NiO catalysts:

$CO + 3\ H_2 = CH_4 + H_2O$

$CO_2 + 4\ H_2 = CH_4 + 2H_2O$

Resulting gas has the composition required for ammonia synthesis: 74% H_2, 24% N_2, and 1% CH_4.

Ammonia synthesis

The chemical reactions for ammonia production occur in the presence of a catalyst according with:

$N_2 + 3H_2 = 2\ NH_3$