**Annex V.4 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-K2CO3. 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 (CO2 removal with K2CO3);
* 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 CO2

Liquid ammonia could be used for:

* Urea production;
* Production of ammonium nitrate (NH4NO3);
* 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*

**NATURAL GAS**

**Ammonia synthesis**

**Purge**

**Flue gas**

**Power**

**Compression**

**Power**

**Preliminary purification (desulphurisation)**

**Waste catalyst**

**Catalyst**

**Primary catalytic reforming**

**Waste catalyst**

**Flue gas**

**Catalyst**

**Steam, fuel**

**Secondary catalytic reforming**

**Waste catalyst**

**Catalyst**

**Air, power**

**Synthesis gas purification (CO2 removal with K2CO3)**

**CO2 desorbtion from**

**K2CO3 solution**

**K2CO3**

**Power**

**Synthesis gas**

**compression**

**Power**

**Synthesis gas**

**methanation**

**Waste catalyst**

**Catalyst**

**AMMONIA**

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 O2 + H2 = H2O

R-SH + H2 = R-H + H2 S

H2S is detained by ZnO catalyst:

H2S+ ZnO = ZnS + H2O

**Catalytic reforming of natural gas**

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

* The primary steam reforming on NiO catalyst:

CH4 + H2O = CO + 3 H2

CO + H2O = CO2 + H2

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

CH4 + 1/2 O2 = CO + H2

CH4 + O2 = CO2 + H2

CO + 1/2O2 = CO2

2H2 + O2 = 2H2O

Obtained gas containing 56% H2, 12% CO, 9% CO2, 22% N2 and CH4 below 0.4%

**Purification of carbon dioxide gas resulting in earlier stages**

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

K2CO3+CO2 + H2O = 2 KHCO3

**Synthesis gas Methanisation**

Residual content of carbon oxides (CO + CO2) is removed by hydrogenation based on NiO catalysts:

CO+ 3 H2 = CH4 +H2O

CO2+ 4 H2 = CH4 + 2H2O

Resulting gas has the composition required for ammonia synthesis: 74% H2, 24% N2, and 1% CH4.

**Synthesis gas compression**

The synthesis gas is compressed to 260 bar; after which it is sent to the ammonia synthesis plant.

**Receiving fresh synthesis gas**

The fresh synthesis gas, after compression, is mixed with the reacted gas from the synthesis column and travels with it to the ammonia cooling circuit.

**Synthesis gas recirculation**

After separating the ammonia from the synthesis gas, it is recompressed at 260 bar.

**Synthesis gas preheating**

The synthesis gas is preheated due to the reacted gas in the synthesis column.

**Ammonia synthesis**

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

N2 + 3H2 = 2 NH3

**Reaction heat recovery**

The heat of the gas leaving the synthesis column is used to obtain 106 bar steam.

**Water cooling of reaction gases**

By cooling with water, the partial condensation of the ammonia contained in the reacted gas is achieved.

**Ammonia cooling of reaction gases**

The final condensation of the ammonia from the reacted gas, mixed with the fresh synthesis gas, is achieved by evaporating a quantity of liquid ammonia.

**Separation of ammonia**

The condensed ammonia is separated from the unreacted gases, which return to the recirculation of the synthesis gas with the following composition: 3 - 4% vol. NH3, 64 - 65% vol. H2, 21 - 22% vol. N2, 7 - 8% vol. CH4, 2 - 3% vol. Ar.

In order to avoid the accumulation of inert gases, a quantity of reacted gas is permanently extracted from the synthesis circuit (continuous purge). After separating the ammonia by cooling with liquid ammonia and washing with water (after washing, ammonia water is obtained), hydrogen is separated from the purge gas by a membrane technology. The resulting hydrogen is recycled to the synthesis compressor suction, and the inert gases (CH4 and Ar) are sent to the primary combustion reformer.