

Ammonia Plant

Author

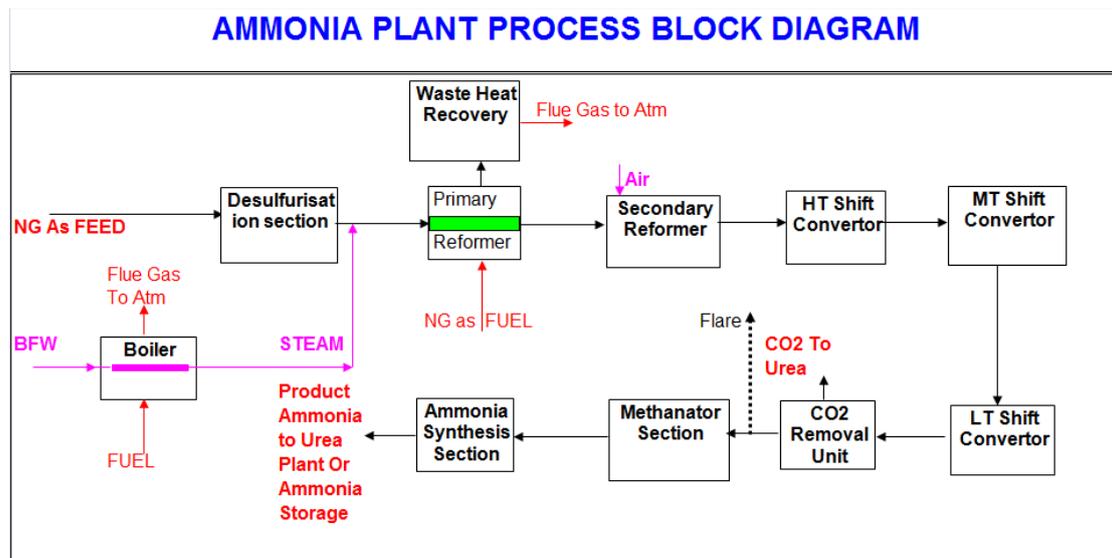


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GENERAL

Ammonia is produced from a mixture of hydrogen (H_2) and nitrogen (N_2), where the ratio of N_2 to H_2 will shall be approximately 3:1. Besides these two components, the synthesis gas will contain inert gases-such as argon (Ar) and methane (CH_4) to a limited degree.:

The source of H_2 is the raw water and the hydrocarbons in the natural gas and naphtha. The source of nitrogen is the atmospheric air.



Ratio between Naphtha and Natural Gas

The ammonia plant is designed for a hydrocarbon feed as natural gas, as well as a mixture of natural gas and naphtha. The maximum ratio between naphtha and natural gas is 1:1. The maximum amount of naphtha can be calculated by the following formula:

$$Q_{pn}(\max) = Q_{ng} \cdot (H_{ng} / H_{pn})$$

where

Q_{pn} is the flow of natural gas in Nm^3/h

H_{ng} is the lower heating value (LHV) of natural gas in Kcal/Nm^3

$Q_{pn}(\max)$ is the maximum flow of naphtha in kg/hr

H_{pn} is the lower heating value (LHV) of actual naphtha in Kcal/kg

Short Description of the Process Units

The process steps necessary for production of ammonia from the above mentioned raw material are as follows:

1. Hydrocarbon feed is completely desulphurized in the desulphurization section.
2. The desulphurized hydrocarbon is reformed with steam and air into raw synthesis gas (process gas) at a pressure $30\text{-}37\text{kg}/\text{cm}^2$ g. The gas contains mainly hydrogen, nitrogen, carbon dioxide and carbon monoxide.
3. In the gas purification section, CO is first converted into CO_2 and H_2 with steam (shift reaction), in order to increase the H_2 yield. The CO_2 is removed in the CO_2 removal section. The residue CO and CO_2 are converted into CH_4 using H_2 (methanation), before the gas is sent to ammonia synthesis loop.
4. The purified synthesis gas is compressed to about $220\text{ kg}/\text{cm}^2$ and sent to the ammonia synthesis loop where it is converted into ammonia.

Short Description of the utility units

Besides the above mentioned process steps, a number of utility function also been installed in order to

- Ensure independency of outside sources other than water, electric power, hydrocarbon feed and fuel
- Meet environment requirements
- Lower consumption of raw materials

1. The naphtha storage unit consists of a day storage tank and associated facilities.
2. The process condensate stripping (unit 33) section removes contaminants such as carbon dioxide, methanol, and ammonia, by direct steam injection before the condensate is sent to the demineralization unit outside the ammonia plant battery limit. The exhaust steam from the process condensate stripper is used as process steam in the reforming section.
3. The steam generation system⁹ (unit 36) provides the HP, MP and LP steam necessary for the various consumers of the ammonia plant, and as an export steam. For startup and emergency backup import of HP steam is foreseen.
4. The cooling tower unit (unit 38), which is a part of the closed cooling water system.
5. The flare system (unit 39) consists of a flare stack and a pilot burner the arrangement. All inflammable gases are sent to the flare headers to a flare stack during startup and shut down in case of any failure in the process line.
6. Demineralized water storage unit (unit 45). The polishing unit (outside ammonia plant) treats the steam condensate from the ammonia plant and returns it as demineralized water to this unit.
7. The effluent treatment unit (unit 46) has been designed to treat or to collect for treatment outside the battery limit of the ammonia plant, various sorts of effluent, such as:
 - Effluent containing chemicals
 - Effluent containing oil
8. The instrument air drying unit (unit 49) provides all other units either in the ammonia plant with dry instrument air. Further up to 2000Nm³/h may be exported for use outside the ammonia plant.

Desulphurization Section

General

The natural gas feedstock that may contain up to 10 ppm (by volume) sulphur compounds must be desulphurized, as the adiabatic prereformer catalyst, as well as the low temperature CO-conversion catalyst are very sensitive to sulphur. For the same reason the naphtha feed, which may contain up to 70 ppm (by volume) sulphur compounds, must also pass through a desulphurization unit. The desulphurization of both natural gas and naphtha takes place in two stages:

- Hydrogenation

- ZnO absorption

The hydrogenation takes place in the hydrogenator, R3201, for natural gas and in R3207 for evaporated naphtha. Both reactors are operating at an inlet temperature of 380°C.

After hydrogenation the two streams are mixed and the H₂O absorption takes place in the ZnO absorbers R-3202 A\B, connected in series.

After desulphurization, the content of sulphur will be less than 0.05 ppm (by volume)

Hydrogenation

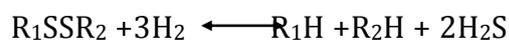
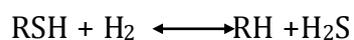
The natural gas feedstock is passed to the preheater coil, E 3204, in the waste heat section, where it is preheated to 380°C before entering the HDS reactor, R3201 (hydrogenator).

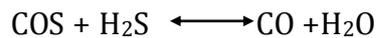
The hydrogen (recycle H₂) required for the hydrogenation is supplied as synthesis gas from the synthesis gas compressor, K 3431, and added to the natural gas downstream the preheater E 3204. The synthesis gas also contains N₂ but this will just act as an inert gas in the front end.

The raw naphtha is deaerated upstream the desulphurization section, it is stripped with natural gas in F 4401 to remove possible dissolved air. Then it is mixed with recycle H₂, to keep the boiling point of the naphtha at a reasonable value before it is evaporated and superheated in E 3215 and H 3203, respectively.

The two HDS-reactors, R 3201 and R 3207, are equipped with one catalyst bed of 3850mm height, containing 9.0 m³ Ni-Mo based catalyst (type TK-251), respectively. The catalyst which are installed as 5mm rings, are especially suitable for hydrocarbons and hydrogenation gas containing carbon oxides, due to low tendency of temporary deactivation.

The catalyst in both reactors makes the following reactions possible:





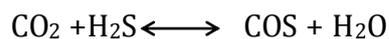
Where 'R' is a radical hydrocarbon.

Besides the above-mentioned reactions, the catalyst also hydrogenates olefins to saturated hydrocarbons and organic nitrogen compounds are to extent converted into ammonia and saturated hydrocarbons.

Operating on natural gas or naphtha containing sulphur, the catalyst will pick up sulphur to 6% by weight when fully sulphided. At this point equilibrium exists between the sulphur in the catalyst and the sulphur in the gas. If the sulphur content of the gas decreases below 1-2 ppm, sulphur will be released from the catalyst.

The most advantages operating temperature of the hydrogenation is between 380 and 390°C. At lower temperature the hydrogenation will not be completed, and at the above temperature of 400°C polymerization products may be formed on the surface of the catalyst .

The presence of the water vapour in the hydrogenated gas will influence the absorption equilibrium composition in the subsequent absorption vessels unfavorably. With CO and CO₂ in the hydrocarbon feedstock or in the recycle H₂, the following reaction will take place in the HDS reactors:



Both reactions are forming water vapour, in order to minimize the formation of water and thereby minimizing the slippage of COS and H₂S from ZnO absorption, the inlet temperature of the HDS reactor should be 380°C. The operating temperature can be used for both the HDS reactors.

High concentration of CO will decompose according to the following reaction:



Carbon formed in this way will deposit inside the catalyst as soot.

When sulphided the methanation activity of TK-251/550 is very low. During initial operation when the catalyst has not picked up any, or only very little sulphur, the methanation reaction may occur with an increase in temperature as a result. If that happens, the hydrogenator inlet temperature shall be decreased to the level necessary for keeping the outlet temperature at 400°C. This may be actual if the natural gas contains 5-6% CO₂ and is sulphur free.

In the sulphided state the catalyst is pyrophoric at temperature above 700°C and it should not be handled unless cooled down to ambient.

Exposure of water to cold catalyst is to be avoided as the absorption of water on alumina carrier of the catalyst may cause a temperature rise of 130-170 °C.

Absorption

The outlet stream from the two HDS-reactors are mixed and the hydrogenated hydrocarbon gas is led to the two ZnO absorbers, R 3202 A and R 3202 B, connected in series.

Each vessel has one catalyst bed with a height of 3600 mm and containing 30 m³ of catalyst, type HTZ-3. The zinc oxide catalyst is installed as 4 mm extrudates and the normal operating temperature is between 350-400°C.

The zinc oxide reacts with hydrogen sulphide and carbonyl sulphide, according to the following equilibrium reactions:



To some extent the zinc oxide will also remove organic sulphur compounds. However, these shall normally be hydrogenated, the equilibrium composition for the reactions between zinc oxide and hydrogen sulphide is expressed by the following equation:

$$P_{\text{H}_2\text{S}} / P_{\text{H}_2\text{O}} = 2.5 \cdot 10^{-6} \text{ at } 380^\circ\text{C}$$

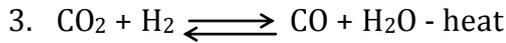
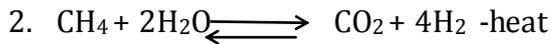
Fresh catalyst or sulphided catalyst reacts neither with oxygen nor with hydrogen at any partial temperature. Zinc sulphided is not pyrophoric and no special care during uploading is required. Steaming operation should not be carried out on R 3202 A/B, the zinc oxide will hydrate and it would consequently not be possible to regenerate the ZnO material in the reactor.

Reforming Section

General

In the reforming section the desulphurized catalytic reforming of the hydrocarbon mixture with the steam and addition of air convert gas into ammonia synthesis gas.

The steam reforming process can be described by the following reaction:



Reaction (1) describes the mechanism of reforming the higher hydrocarbons, which are reformed in stages to lower and lower hydrocarbons, finally resulting in methane, which is reformed according to reaction (2). The reverse shift reaction (3) requires only little heat, whereas the heat required for reaction (1) and (2) will quite dominate the picture.

The reaction takes place in two steps when natural gas is the feedstock and in three steps, when natural gas mixed with naphtha is the feedstock. In the scheme below the steps are listed:

Type of feedstock	Reforming steps
Natural gas	Primary reforming
	Secondary reforming
Mixed feed	Adiabatic prereforming
	Primary reforming
	Secondary reforming

When the ammonia plant is fed on natural gas only the adiabatic prereformer, R3206, will be bypassed.

Carbon Formation

In operation of reforming system, carbon formation outside and/or inside the catalyst particle is possible. Carbon deposits outside the particle will increase the pressure drop over the catalyst bed and deposits inside will reduce the activity and mechanical strength of the catalyst.

In operation of the adiabatic prereformer, carbon deposit is possible only in the case of very low steam/carbon ratio ($<<2.5$) and overheating of the feed ($>520^\circ\text{C}$).

In the tubular reformer, carbon formation is not possible under the foreseen conditions. However if the catalyst is poisoned, for instance by sulphur, it will lose activity and carbon formation will occur. Also if the carbon is insufficiently

reduced, or if it has become partly oxidized during production setups without subsequent reduction, carbon formation may take place.

As for the adiabatic prereformer, a too low steam/carbon ratio may cause carbon formation in the tubular reformer. This would result in carbon lay down, especially inside the catalyst particle.

The design ratio used in the present unit is water/carbon=3.3 and is sufficiently above the ratio where carbon formation on an active catalyst is possible.

Reaction Heat

In the primary reformer, the necessary heat of reaction is supplied as indirect heat by firing, and in the secondary reformer the heat is supplied as direct heat by combustion of the gas mixture with air. The introduction of air at the same time provides the nitrogen required for ammonia synthesis. Since the hydrogen/nitrogen ratio in the purified synthesis gas should be maintained at a value close to 3.0, the amount of air is fixed. Overall the reforming reaction and methane leakage from the secondary reformer is controlled by adjusting the firing of the primary reformer.

Operating Pressure

As methane acts as an inert gas in the ammonia synthesis, it is desirable to reduce the methane content of the raw ammonia synthesis gas to the lowest possible level, in order to keep the level of the inert gas low. The methane content in the synthesis gas is governed by the equilibrium at the reforming reaction (2), and by the approach obtainable in practice, depending on the catalyst activity. According to the reaction (2), lower methane content will be obtained by increasing the temperature, lowering the pressure and by adding more steam.

On the other hand, a relatively high reforming pressure results in considerable savings of the power consumption for the synthesis gas compression. An operating pressure of approximately 34kg/cm²g inlet of the primary reformer gives a reasonable economic compromise. If the adiabatic prereformer is in line due to naphtha in the feedstock, the pressure inlet E 3201 will be 35.8kg/cm²g.

Adiabatic Prereformer

The hydrocarbon feed from the desulphurization section is mixed with process steam and preheated in a coil, E3201, installed in the flue gas waste heat section of the primary reformer. The inlet temperature to R 3206 should be 490°C.

All the higher hydrocarbons are virtually decomposed into methane by steam reforming by means of the prereformer catalyst. The prereformer contains two catalyst beds loaded with a total 23.4 m³ catalyst (type RKNGR-7H), the first bed with a height of 2350 mm, and the second bed with a height of 1450 mm.

Primary Reformer

In the case of natural gas used as feedstock, the first step of the steam reforming process takes place in the primary reformer, H 3201. In the naphtha case the outlet gas feeds H3201 from the adiabatic prereformer, R 3206. In H 3201 the hydrocarbon and steam mixture, which is preheated to 485-490°C, is passed downwards through vertical tubes containing catalyst. The primary reformer is a fired heater where the sensible heat and heat of reaction are transferred by radiation from a number of wall burners to the catalyst tubes. In order to ensure complete combustion of the fuel gas the burners are operated with an excess air ratio of about 5%, which corresponds to 0.9% of oxygen in the flue gas.

The hydrocarbons in the feed to the primary reformer are converted into hydrogen and carbon oxides. The outlet gas leaving the primary reformer contains approximately 10-11% of methane (on dry basis). The exit temperature of the primary reformer is about 800°C, which is also the inlet temperature to the second step of the reforming. The primary reformer has a total of 288 reformer tubes installed in two radial sections and loaded with 42.8 m³ of catalysts. The upper part of the reformer tubes is loaded with prereduced catalyst, R-67-7H. The normal size is 16*11 mm.

Reduction of the Catalyst

Activation of the R-67-7H catalyst is carried out means of hydrogen during initial start-up of the reformer. The anticipated source of hydrogen for reduction purpose is methane, which in the presence of steam will be converted in the upper part of the tubes at a temperature ranging from 485 °C (at the top of the reformer tubes) to 800°C (at the bottom of the reformer tubes). The formed hydrogen is now reduces the nickel oxide content of R-67-7H to metallic nickel and the reduction progresses down through the catalyst tubes. The temperature required for the reduction is 600°C. During the reduction of the catalyst it is recommended to operate with a steam/carbon ratio equal to approx. 6-8. As alternative hydrogen source, recycle gas from the existing ammonia plant (Ammonia 1) may be used.

Maintaining the Reformer Catalyst

In order to maintain the high activity, excessive steaming of the catalyst at elevated pressure and/or temperature should be avoided to the extent possible.

As already mentioned, sulphur is a severe poison to the reformer catalyst. Sulphur reacts with the metallic nickel, forming nickel sulphide. This causes deactivation of the catalyst, and consequently a risk of carbon formation. Carbon formation is not possible when operating the primary reformer at the chosen conditions. If, however, the catalyst loses activity, due to poisoning, maloperation or ageing, carbon formation may occur. Carbon formation itself decreases the activity of the catalyst. Therefore it is very important to take immediate action in order to prevent further formation.

Carbon deposits usually increase the pressure drop across the reformer and hot bands may be observed on the reformer tubes. Another consequence of carbon formation is that the catalyst particles lose their mechanical strength.

If the hydrocarbon feed has a high content of olefins, aromatics or naphthenes, they may cause carbon formation. The latter components, however, do not normally appear in natural gas. As for the mixed feed case they are converted in the adiabatic prereformer. Furthermore, it is important not to operate the reformer with too low carbon ratio, as this gives a thermodynamically possibility for carbon formation, especially inside the catalyst particles.

After slight sulphur poisoning, operating the reformer for a few hours with sulphur free feed may restore the activity. A severe sulphur poisoning requires a special regeneration procedure. Also salt droplets present in the steam, for instance, NaCl and Na₃PO₄ and components containing heavy metals are poisonous to the catalyst.

Secondary Reformer

In the secondary reformer, R 3203, the process air is mixed with air. The partial combustion takes place in top part of R 3203 and causes a considerable increase in temperature. From the "combustion chamber" the gas passes down through a

catalyst bed where the last part of the reforming takes place with simultaneous cooling of the gas. The temperature of the process gas leaving the secondary reformer is about 990°C and the methane concentration is approx. 0.30 mole % (on dry basis). The exit gas from the secondary reformer contains about 13% CO and 7.3% CO₂ and consequently there is a theoretical risk of carbon formation according to the Boudouard reaction.



When the gas is cooled at the actual operating conditions the carbon formation can only take place at a temperature below 721°C outlet primary reformer and below 776°C outlet secondary reformer, because of the equilibrium conditions. The lower limit for the reaction is 650°C as the reaction rate becomes too slow at lower temperatures.

Cooling of the process gas is carried out in the waste heat boiler, E 3206, where the exchange heat is used for production of the high pressure steam necessary in the ammonia plant. The boiler is designed to obtain a rapid cooling but a too high heat flux is to be avoided, as it may cause film boiling on the steam side, which in turn would decrease the heat transfer coefficient. The secondary reformer, R 3203 has been charged with a total of 39m³ of RKS-2-7H catalyst. The dimensions of the catalyst are 20mm*18mm high, with seven holes.

The combustion of the process air with air gives a temperature of 1100-1200° C in the upper pan. As the reformer reaction of methane absorbs heat, the outlet temperature of the secondary reformer is approx. 990°C. In the temperature range 1400-1500°C, the catalyst starts sintering.

Gas Purification Section

The gas leaving the reformer section will have the following composition range expressed in volume percent on dry basis:

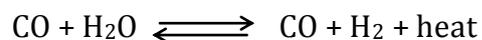
Hydrogen	= 55.6-56.4 mole%
Carbon monoxide	= 13.0-13.8 mole%
Carbon dioxide	= 7.3-8.7 mole%
Nitrogen	= 22.3-22.7 mole%
Argon	= 0.3 mole%
Methane	= 0.3 mole%

Further, the gas contains water vapour corresponding to a steam on dry gas ratio at about 0.527-0.559. Of the above components argon is an inert gas introduced with the process air.

The purpose of the gas purification section is to prepare a synthesis gas containing hydrogen and nitrogen in the ratio 3:1 and besides this only containing inert gases like methane and argon in the lowest possible concentration. The gas purification section comprises three main component steps:

1. CO-Conversion
2. CO Removal (the GV Section)
3. Methanation

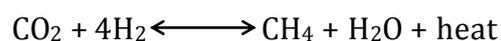
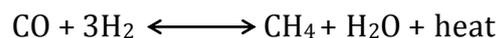
Carbon monoxide is converted in the two shift converters, R 3204 and R 3205, according exothermic reaction:



The reacted gas will contain only about 0.3% CO (on dry basis). The reacted part of the CO increases the H₂ yield with simultaneous formation of CO₂, which is easier to remove.

After the cooling of the gas and condensation of the main part of the water content, the CO₂ is removed in the CO₂ removed unit, so that less than 0.03% CO₂ remains.

Even the small amount of CO and CO₂ left are strongly poisonous to the ammonia synthesis catalyst and should therefore be removed down to a concentration of a few ppm. This is done in the methanator R 3311, where the reverse reforming reaction will takes place:



Thus resulting in formation of methane at the expense of hydrogen.

The purpose of the gas purification section is to keep the methane concentration reasonably low, as nothing can be done to decrease the content of the other inert gas, argon.

Shift Section

General

The process gas leaving the reforming section contains approximately 13.0 vol % carbon monoxide which is converted into carbon dioxide and hydrogen by means of the shift reaction:



The shift reactions is favoured by lower temperature and more water vapour, while the reactions rate increases with higher temperature. The outlet temperature for the shift reactions, which depends on the activity of the catalyst and quantity of the gas handled.

The shift reaction takes place in the two CO converters, R 3204 and R 3205 with gas cooling after each converter.

During normal operation, the following conditions prevail:

Units	Temp. in °C	Temp. out in °C
R 3204	350-370	420-440
R 3205	200-210	215-230

High Temperature CO-Conversion

The high temperature CO-converter, R 3204 contains a total of 92.28 m³ of SK-201-2 catalyst in two beds, each 2350 mm high. The catalyst is chromium oxide promoted iron oxide, in the form of pellets 6 mm high and 6 mm in diameter.

The catalyst has been installed in its highest oxidized state and the reduction (activation) is carried out by means of process gas containing hydrogen .the reduction will takes place as a temperature range from 250°C to 350°C.

The activated SK-201-2 catalyst may be continuously operated in the range of 330-470°C.

Initially ,the catalyst operates at a gas inlet temperature of about 350°C later the optimum inlet temperature will be higher , but as long as the outlet temperature has not reached 460°C,the activity will decrease only slowly.

Chlorine and inorganic salts are poisons to the catalyst. The content of chlorine in the gas should be will below 1 ppm. However since the reforming and low temperature shift catalysts are much more sensitive to these contaminants, they

are always removed to a level will below the tolerance limit of the SK-201-2 catalyst.

The catalyst is not affected by sulphur in the quantities present in the plant. The fresh catalyst contains, however, a small amount of sulphur as sulphate, which will be depleted as H₂O during the first 36-48 hours of operation.

Heating in condensing steam will not harm the SK-201-2 catalyst in any way. However the hot catalyst should not be exposed to liquid water, since it may disintegrate the catalyst. As the activated catalyst is pyrophoric, it shall be handled with care during unloading.

Low Temperature CO-Conversion

The low temperature CO converter contains 122 m³ catalyst in two beds, which are 3.36 and 2.85m high. It is foreseen to place a layer 6.1 m³ chromium based catalyst on top of the first bed, which will act as a chlorine guard catalyst, while the remaining 115.9 m³ will be made up of alumina based catalyst. The catalyst consists of oxides of copper, zinc, and chromium or alumina.

As the catalyst is extremely sensitive to sulphur which may be liberated not only from the upstream HTS catalyst but also to a certain extent from the brick lining and the secondary reformer catalyst during the first period of operation, the LT shift is by passed during this stage, until the gas is practically free from sulphur.

Besides sulphur, also chlorides and gaseous Si compounds are severe poisons. In order to give an idea of the poisoning effect of such compounds on the catalyst, it is indicated the activity of the catalyst will be minimized considerably by a sulphur pick up 0.2 wt % and by a chlorine content 0.1 wt %. The catalyst is activated at 150-200°C in nitrogen containing 0.2-2 wt % hydrogen.

During the reduction the copper oxide reacts with the hydrogen under formation of free copper.

Under no circumstances the hot LK-801-S catalyst must be exposed to liquid water, as this would disintegrate the catalyst.

As the catalyst is pyrophoric in its reduced state, special precautions have to be taken during unloading.

<i>Bed no.</i>	<i>height</i>	<i>catalyst</i>
1 st bed	3360 mm	6.1 m ³ LSK +59.9 m ³ LK-801-S
2 nd bed	2850 mm	56 m ³ LK-801-S

The LK-801-S catalyst is operating in the temperature in the range of 170-250°

Carbon Dioxide Removal Section

General

Basically, the CO₂ removal section compromise one absorber (F 3303), where the CO₂ content in the process gas will be absorbed in a liquid phase at a high pressure.

The liquid containing the CO₂ is transferred to a two tower regeneration unit (F 3301 and F 3302). In two towers the pressure is low and thereby, due to equilibrium, the CO₂ again will be transferred into the gas phase.

Carbon dioxide is removed by absorption in the hot aqueous potassium carbonates solution containing approx 30 wt% potassium carbonate (K₂CO₃) partly converted into bicarbonate (KHCO₃). The solution further contains activators, glycine, and a Diethanole amine (DEA), and vanadium oxides as corrosion inhibitor. The reason for keeping the solution hot is to increase the rate of absorption and keep the bicarbonate dissolved. Another advantage is that the temperature is approximately the same in the absorber and in the regenerators, i.e. the boiling point temperature of the solution at the pressure prevailing in each of the two regenerators. Thus, it is not necessary to supply heat to the solution before the regeneration.

The process gas from the shift reactors is passed to the CO₂absorber, F 3303, which contains stainless steel packing material distributed in 5 beds.

In the absorber, the gas flows upwards against a descending stream of potash solution. Approximately 15% of the solution is introduced above the top bed at 70°C, where the remainder is introduced at about 106°C below the two top beds.

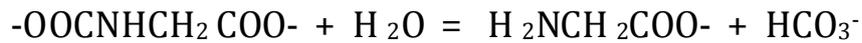
The CO₂ absorption occurs according to the following reaction mechanism:

1. $\text{CO}_2 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+$
2. $\text{CO}_3^{--} + \text{H}_2\text{O} = \text{HCO}_3^- + \text{OH}^-$
3. $\text{CO}_3^{--} + \text{CO}_2 + \text{H}_2\text{O} = 2\text{HCO}_3^-$

The reaction rate of 3 is determined by 1 which is the slower step of 1 and 2. The activators action resulting in an increased rate is caused by the quick transfer of gaseous CO₂ into the liquid phase by means of the glycine formation according to the reaction:

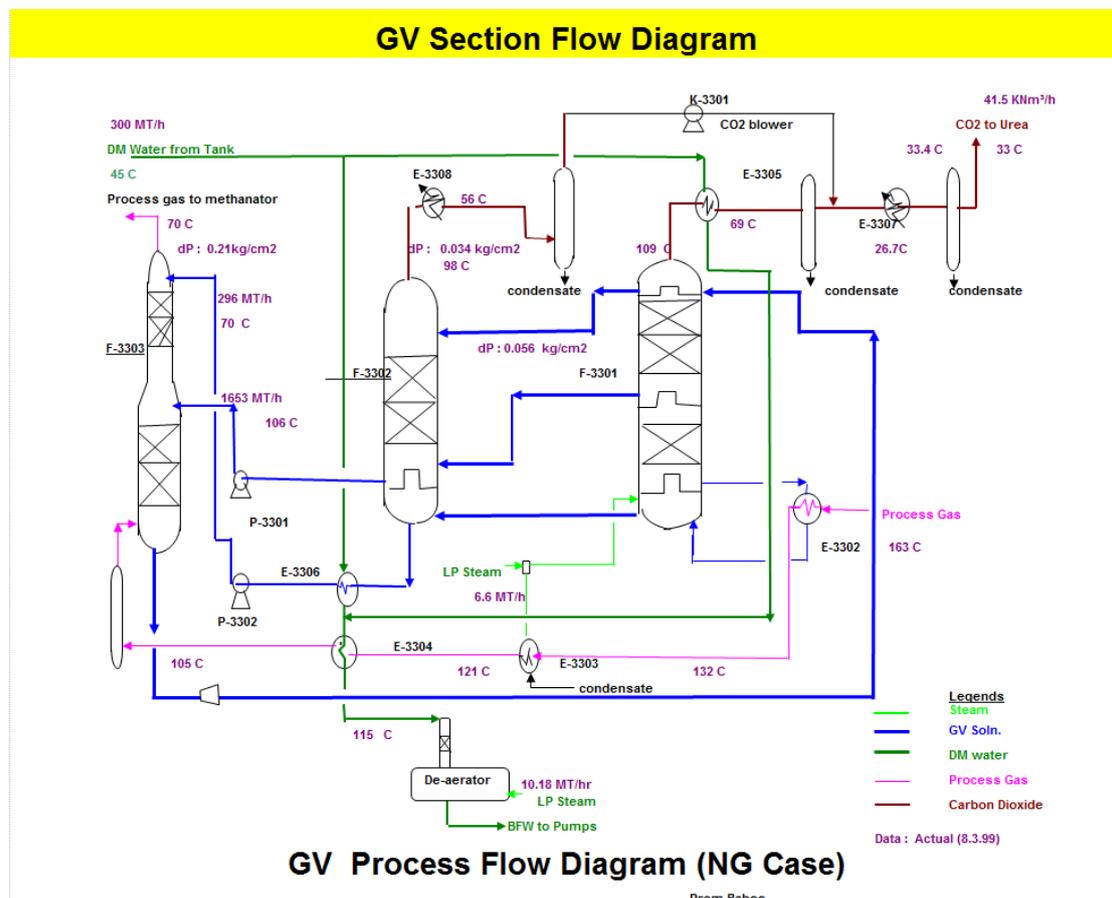


The activators effect is much higher than the one relating to carbamate concentration. At high temperature and in the presence of OH, the carbamate is hydrolyzed and the activator is restored according to the reaction:

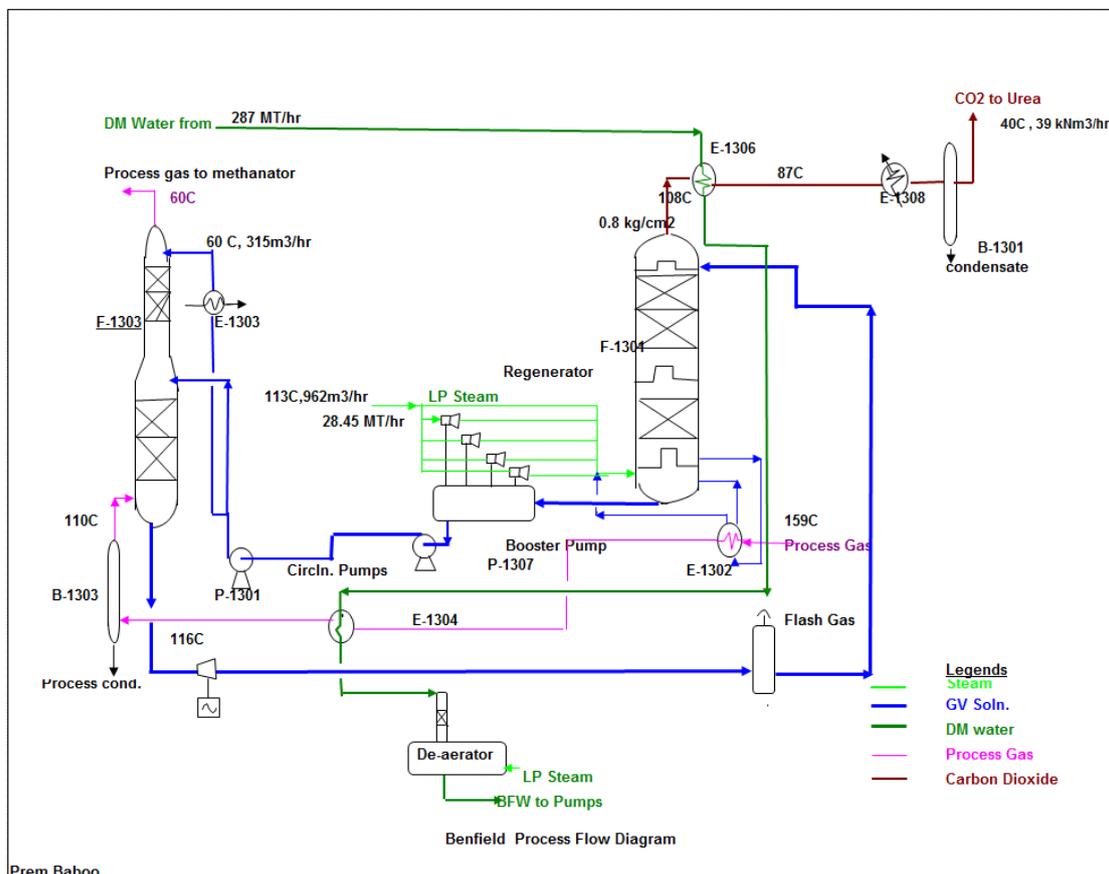


The sum of 4 and 5 gives 1. As reaction 4 and 5 takes place continuously, it means that the glycine acts as a CO₂ carrier. Reaction 5 is the hydrolysis of the glycine carbamate. This reaction is catalyzed by a small amount of DEA in the solution.

The absorption takes place in two stages in F 3303. In the first stage (the lower part of F 3303), where the bulk of CO₂ is absorbed, the high temperature increases the reaction rate of 5 and 3. This is done by using the normal regenerated solution (semilean solution) from F 3302.



In the second stage, a stream of strongly regenerated solution (lean solution) is utilized. At the lower temperature, the CO₂ vapour pressure of the solution is further reduced to meet the low CO₂ slippage in the purified gas (about 0.03 wt % dry CO₂).



The solution leaving the absorber bottom is loaded with CO₂ and will be reformed to as the rich solution. The rich solution is desulphurized through the hydraulic turbine, TX 3301. The shaft power from the hydraulic turbine is used to drive the semilean solution pump, P 3301.

From the hydraulic turbine the rich solution enters the top of the first regenerators F3301. The pressure is reduced to 1.0 kg/cm² g.

A steam of rich solution extracted from the top of F 3301 is depressurized through a control valve and enters the top of the LP regenerator, F 3302, working at low pressure (0.1 Kg/cm g).

The level of regeneration is expressed by the fractional conversion. Defined as

$$X = \frac{1}{2} \frac{(C_{\text{HCO}_3^-})}{C_{\text{HCO}_3^-} + C_{\text{CO}_3^{2-}}}$$

$$F_C = \frac{\text{KHCO}_3 \text{ (as K}_2\text{CO}_3\text{)}}{\% \text{ eq. K}_2\text{CO}_3}$$

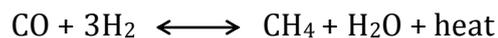
The highest X-value is at bottom of the absorber, where the solution on its way down the absorber tower has been in contact with the process gas. The lowest value of the fractional conversion is at the bottom of the regeneration tower where CO₂ has been stripped off through the packed beds in the towers.

Methanation

General

The final part of the gas purification is the methanation where residual carbon dioxide are converted into methane, which acts like an inert gas in the ammonia synthesis loop. As previously mentioned, the carbon oxides (CO and CO₂) are serve poisons to the ammonia synthesis catalyst.

The methanation takes place in the methanator, R 3311, and the reactions involved are the reverse of the reforming reactions:



The determining parameters for the methanation reactions are besides the activity of the catalyst:

- Temperature
- Pressure
- And the steam content of the process

Low temperature, high pressure and low steam content tend to favour the methane formation.

Within the recommended temperature range 280 to 400 °C, the equilibrium conditions are, however, so favourable that it is practically only catalyst activity which determines the efficiency of the methanation. The activity of the catalyst increases with increasing temperature, but the lifetime of the catalyst is shortended.

As indicated above, the two methanation reactions are exothermic and in normal operation the temperature rise is in order of 20 °C.

Methanation Catalyst

The methanator, R 3311, has been provided with two catalyst beds. Each 2650mm high, containing a total of 60 m³ catalyst. Initially only the upper bed will be loaded with 30 m³ PK- 5 catalyst. The catalyst is a nickel catalyst containing approx. 27% nickel.

The methanation reaction starts at about 250 °C, causing a temperature increase in the catalyst beds. The increase of temperature depends on the contents of CO and CO₂ in the process gas. The temperature increase will be approx. 60 and 75 per % CO₂ and % CO converted, respectively.

In order to ensure sufficiently low content of CO and CO₂ in the effluent gas, the inlet temperature will typically be within 290 to 320 °C depending on the catalyst activity and gas composition. The methanation catalyst should not be exposed to temperature above 420°C for extended period of time. The catalyst is very sensitive to arsenic, sulphur and chlorine compounds.

Steam without hydrogen will oxidize the catalyst and should therefore not be used for heating, cooling, or purging. Furthermore, the catalyst should not be exposed to condensing steam, as it will disintegrate.

Deactivation of the catalyst may be due to:

- Thermal ageing, due to high concentration of CO and CO₂ in the inlet gas, to R 3311.
- Gradual poisoning by impurities in feed gas.
- Malfunctioning of the CO₂ removal system (GV section) resulting in carryover of absorption liquid.

During the catalyst lifetime it will lose some activity, which is compensated for by increasing the inlet temperature.

Simply heating in normal process gas carries out catalyst activation. The content of CO and CO₂ in the gas used during activation should be as low as possible, preferably below 2 mol% CO+CO₂ in order to minimize the temperature rise.

Process Description

The inlet temperature at the normal operating conditions is 320°C. The process gas is heated to this temperature partly by passing through a feed/effluent/gas-gas exchanger, E 3311, and partly through E 3209, a trim heater. The process gas composition will have a temperature increase of 18-19°C corresponding to an outlet temperature of 339°C. The gas/gas exchanger, E 3311, cools the purification of gas to 92°C. To remove as much water as possible from the purified gas, it is further cooled to 38°C by the final gas cooler, E 3312. The condensate is separated from the purified gas in the final gas separator, B 3311.

The purified gas outlet, B 3311, contains N₂, H₂ and approximately 1 mol% of inert as Ar, CH₄ and H₂O. The ratio of H₂ to N₂ is approximately 3:1.

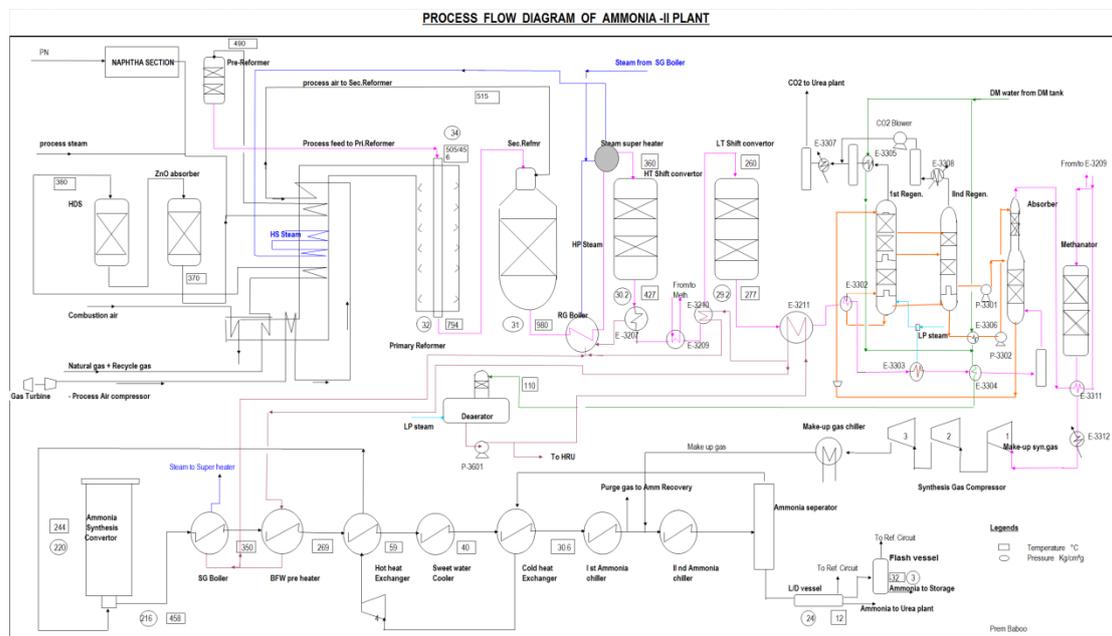
Ammonia Synthesis Section

General Process Description

The ammonia synthesis takes place in the ammonia synthesis converter, R 3501, according to the following reaction scheme:



The reaction is reversible and only a part of the hydrogen and nitrogen is converted into ammonia by passing through the catalyst bed. The conversion of the equilibrium concentration of ammonia is favored by high pressure and low temperature. In R 3501 only about 30% of the nitrogen and the hydrogen are converted into ammonia.



To get maximum overall yield of the synthesis gas, the unconverted part will be recycle to the converter after separation of the liquid ammonia product.

After the synthesis gas has passed through R 3501, the effluent gas will be cooled down to a temperature which the main part of the ammonia is converted.

The circulation is carried out by means of the recirculator, which is an integrated part of the synthesis compressor, K 3431.

As the reaction rate is very much enhanced by high temperature, the choice of temperature is based on a compromise between the theoretical conversion and the approach to equilibrium.

The ammonia synthesis loop has been designed for a maximum pressure of 245kg/cm² g. The normal operating pressure will be 220kg/cm² g depending on load and catalyst activity.

The normal operating temperatures will be in range of 360-525°C for the 1st bed and 370-460°C for the 2nd bed.

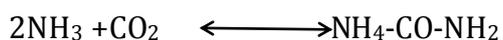
The heat liberated by the reaction (about 750kcal/kg produced ammonia) is utilized for high pressure steam production (in the loop waste heat boiler, E 3501) and preheat of high pressure boiler feed water.

As illustrated in diagram, the converted effluent gas is cooled stepwise, first in the loop waste heat boiler, E 3501, from 456-350°C. Next step is cooling to about 269°C in the boiler feed water preheated, E3502. And then the hot heat exchanger, E 3503, where the synthesis effluent gas is cooled to 61°C by preheating of converter feed gas.

The synthesis gas is cooled to 37C in the water cooler, E 3504 and to 28 C in the heat exchanger.

The final cooling to 12°C takes place in the ammonia chillers. The condensed ammonia is separated from the circulated to the ammonia converter through the cold heat exchanger, the recirculator, and the hot heat exchanger.

The water vapour concentration in the make-up gas is in the range of 200-300 ppm, depending on the operating pressure in the loop. The water is removed by absorption in the condensed ammonia. The carbon dioxide in the make-up gas will react with both gaseous and liquid ammonia, forming ammonium carbamate:



The formed carbamate is dissolved in the condensed ammonia. As the water deactivates the ammonia synthesis catalyst, the content of carbon monoxide in the make-up synthesis gas should be kept as low as possible.

Inert Gases

The make-up gas enters the loop between the two ammonia chillers. This gas contains small amount of argon and methane. These gases are inert in the sense that they pass through the synthesis converter without undergoing any chemical changes. The inert will accumulate in the synthesis loop, and a high inert level, i.e. high concentration of inert gases will build up in the circulating synthesis gas. The inert level will increase until the addition of inert gases will make the make-up gas in the same as the amount of inert removed from the top.

The low temperature outlet of the 1st ammonia chiller means that the partial pressure of ammonia in the gas phase is relatively low. Only a minor amount of ammonia will be removed together with the purge gas. The purge gas is further cooled in the purge gas chiller, E 3511, and the liquid ammonia is separated in B 3512. The liquid ammonia is sent to B3501.

Hydrogen/Nitrogen Ratio

By the synthesis reaction, 3 volumes of hydrogen reacts with 1 volume of nitrogen to form 2 volumes of ammonia.

The synthesis loop is designed for operating at H₂/N₂ ratio of 3.0, but special conditions may make it favorable to operate at a slightly different ratio in the range of 2.5-3.5. When the ratio is decreased to 2.5, the reaction rate will increase slightly, but decrease again for ratios below 2.5. On the other hand the circulating synthesis gas will be heavier. Therefore, the pressure drop and ammonia concentration at the inlet of the ammonia synthesis converter will increase.

Ammonia Converter R 3501

Flow Pattern in R 3501

At the top of the converter, the gas passes the tube side of the inter bed heat exchanger, where the inlet gas is heated up to the reaction temperature of the heated up the reaction temperature of the 1st catalyst bed by the heat exchanger with gas leaving the 1st catalyst bed. The gas inlet temperature to the 1st bed is adjusted by means of the so-called "cold shots" which is cold synthesis gas introduced through the transfer pipe of the center tube.

The gas, which leaves the 1st catalyst bed, is led through the 2nd bed and into the center tube from which it is returned to the ammonia loop.

The two catalyst bed contains a total of 109.3 m³ of KMIR catalyst, which is a promoted iron catalyst containing small amounts of non-reducible oxides.

Reaction Temperature

At the inlet of R 3501, 1st catalyst bed, the minimum temperature of approx. 360°C is required to ensure a sufficient reaction rate. If the temperature at the catalyst inlet is below this value, the reaction rate will become so low that the heat liberated by the reaction becomes too small to maintain the temperature in the converter. The reaction will quickly extinguish itself if properly adjustments are not made immediately.

On the other hand, it is desirable to keep the catalyst temperature as low as possible to prolong the catalyst life. Therefore, it is recommended to keep the catalyst inlet temperature slightly above the minimum temperature. It is anticipated that the synthesis gas enters the 1st catalyst bed at a temperature of max. 400°C. As the gas passes through the catalyst bed the temperature increases to a maximum temperature in the outlet from the 1st bed, which is normally the highest temperature in the converter, called the “hot spot”. The temperature of the hot spot is upto 510°C, but should not exceed 520°C. The gas from the 1st bed is cooled with some of the cold inlet gas to the 1st bed in order to obtain a temperature of approx. 370°C inlet 2nd bed. The gas outlet temperature from the 2nd bed is about 455°C.

Catalyst

The catalyst is distributed with 29.0 m³ in the first (upper) bed, and 80.3 m³ in the second (lower) bed. The particle size of the catalyst is 1.5-3 mm. The smallest particle size causes a very high overall catalyst activity. Further the radial flow design of the converter allows small particle without causing a prohibitive pressure drop.

The pre-reduced KMIR catalyst has been stabilized during manufacturing by superficial oxidation. The partly oxidized catalyst contains about 2 wt% of oxygen.

The stabilization makes the KMIR catalyst non pyrophoric up to 90-100°C, but above 100°C the catalyst will react with oxygen and heat up spontaneously.

Reducing the iron oxide surface layer to free iron with simultaneous formation of water activates the catalyst. The reduction is carried out with circulating synthesis gas. The desired level temperature is obtained by using the startup heater, H 3501

The use of synthesis gas with hydrogen to nitrogen ratio close to 3:1 for activation of KMIR has two advantages.

The first is production of ammonia starts early, causing a heat production. The production of heat provides the possibility of circulating more synthesis gas, which helps in reducing the remaining part of the catalyst.

The second advantage is removal of the formed water from the circulating gas. It will be dissolved in ammonia and then purify the circulating the synthesis gas. This is important as water is the catalyst poison. The catalyst activity decreases

slowly during normal operation and the catalyst lifetime, which is normally more than 5 year, its affected by the actual process conditions, notably the temperature in the catalyst bed and the concentration of the catalyst poisons in the synthesis gas at the inlet of the convertor.

Although the KMIR can be used in the range of 530-550°C ,it should be noted that the lower the catalyst temperature are in operation, the slower the decrease in catalyst activity will be , and accordingly the lifetime will be prolonged. It is therefore recommended to maintain the lowest possible catalyst temperature during operation, especially for the 2nd bed which determines the conversion.

All compounds containing oxygen, such as water, CO and carbon dioxide, are poisonous gas is clean again. But as some permanent deactivation will take place, high concentrations of oxygen compounds at the convertor inlet, even of short duration, should be avoided.

Sulphur and phosphorous compounds are severe poisons, as the catalyst deactivation will be permanent. A probable source of introduction of such contaminants is the seal oil.

Refrigeration

The purpose of refrigeration circuit is to carry out the various cooling tasks in the ammonia synthesis loop. The primary task is to condense the ammonia, which is produced in the convertor. Other cooling tasks are cooling of make-up gas, purge gas, let-down gas, and inert gas.

6 chillers operating at three different pressure (3 “chillers levels”),

- A refrigeration compressor,
- An ammonia condenser,
- And an accumulator.

Besides the above-mentioned equipment the refrigeration circuit includes the following. Three K.O drums (one for each compressor stage), to protect the refrigeration compressor of droplets of ammonia.

A flash vessel, from where the makeup ammonia is fetched and the spent ammonia is returned to from the refrigeration circuit.

The first ammonia chiller, E 3506 and the make-up gas chiller, E 3514 operate at the highest level which is a temperature of 18.8°C, corresponding to a pressure of 7.8 Kg/cm²g. The second ammonia chiller, E 3507, operates at the medium level, where the ammonia boiling temperature is 6.9°C with a corresponding pressure of 4.6Kg/cm²g.

The three chillers: purge gas chiller, E 3511, let down gas chiller, E 3508, and the inert gas chiller, E 3509, operate at the lowest chiller level, where the ammonia boiling temperature range from -33 to -30°C and the corresponding pressure is approximately 0.05 kg/cm²g.

Ammonia Wash Section

General

The ammonia wash section removes and recovers the major part of the ammonia contained in the off gas, let down gas, and the inert vent gas from the loop.

- The purge gas steam is taken out from the loop just after the 1st ammonia chiller, E 3506. Still under pressure the gas is cooled down to -25°C in the E 3511. Some of the ammonia is separated as liquid. The gas fraction from the separation is sent to the purge gas absorber, F 3522.
- In order to avoid accumulation of inerts in the refrigeration section, a purge flow of the non-condensable gases is sent to the inert gas chiller, E3509, where they are cooled further to about -25°C. At this temperature some of the ammonia is removed as liquid. The gas fraction from the separator is sent to the off gas absorber, F 3523.
- The letdown gas is produced in the letdown vessel. The liquid ammonia from B 3501 is sent to the letdown vessel B 3502. The main part of the dissolved gases will be released due to the pressure reduction from the loop pressure of 209kg/cm²g to pressure in the letdown vessel of 26kg/cm²g. At this pressure the gas is cooled to -25°C in E 3308. Some of the ammonia is separated as liquid. The gas fraction from the separation is sent to the off gas absorber, F 3523.

The let down and inert gas is mixed before entering the ammonia wash section.

Off Gas Absorber, F 3523

The off gas containing ammonia is introduced at the bottom part of the off gas absorber, F 3523, where it is washed in counter-current with water introduced at the top of the absorber. The purified off gas leaving the absorber at the top contains approxi 0.02mole % ammonia, whereas the ammonia water solution leaving the absorber at the bottom contains approximately 10 mole% ammonia. Operating pressure is 81 kg/cm²g.

The absorber, F 3523 has been provided with two beds, each of 2500 mm height, containing 1 “pall rings (2*0.22 m³)

Purge Gas Absorber, F 3522

The purge gas containing ammonia is introduced at the bottom part of the purge gas absorber, F 3522, where it is washed in counter-current with water introduced at the top of the absorber. The purified off-gas leaving the absorber at the top contains approximately 0.01 mole ammonia, whereas the ammonia water solution leaving the absorber at the bottom contains approximately 18 mole % ammonia. Operating pressure is 15 kg/cm²g.

The absorber, F 3522 is provided with 20 trays, to ensure a good contact between the liquid and vapour phase.

Distillation:

The ammonia water leaving the absorber is mixed. The ammonia solution is sent through the rich/lean solution exchanger, E 3523, where the solution is preheated to about 163°C and into the distillation column, F 3521. The column has been provided with 20 trays, to ensure a good contact between the liquid and the vapour phase.

The necessary heat for the distillation is provided from the above mentioned preheating and from the reboiler, E 3521, where heat is provided by condensing medium pressure steam (38 kg/cm²g, 266°C).

From the bottom of F 3321 lean solution is returned to the absorber, after passing the rich/lean solution exchanger, E 3523, and the lean solution cooler, E 3524. After cooling, the temperature of the lean solution is about 43°C.

The distillation is carried out at a pressure of 25 kg/cm²g. The temperature of the gaseous ammonia, which leaves the top of the distillation column, is about 60°C. This means that the water content in the ammonia is less than 0.1 vol % .The gaseous ammonia is condensed in the ammonia condenser, E 3522. The major part of the product ammonia is returned to the distillation column as reflux. The rest of the liquid ammonia is sent to ammonia storage.

Due to the losses of water in the purified gaseous and in the product ammonia, it is necessary with a small water make-up flow. The flow is taken as condensate from the tube side of the reboiler, E 3521.

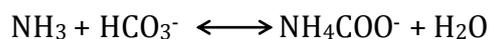
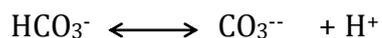
The purified gases leaving the top of the absorber contain H₂ and CH₄. The fuel gas is used for firing in the primary reformer 3201.

Process Condensate Stripping Section

General

Process condensate which is separated from the synthesis gas produced in the front end as well as excess condensate from the GV unit is purified in the process condensate stripper, F 3321.

During operation of the ammonia plant, small amounts of ammonia are formed in the secondary reformer and small amounts of methanol are formed in the low temperature CO-converter. Together with carbon dioxide present in the raw synthesis gas, these compounds enter the process condensate according to the following equilibrium reactions:



The methanol is physically dissolved in the process condensate.

In order to reduce the consumption of regeneration chemicals in the demineralization unit, the above mentioned compounds are stripped off by means of steam.

The process condensate stripper operates at a pressure of 38 kg/cm² g. The overhead stream from the process condensate stripper is returned to the front end and used as process steam for the reforming section. In the reforming section methanol and ammonia will undergo chemical reaction and end up as nitrogen, hydrogen and carbon dioxide.

The stripped condensate is cooled approximately to 125°C in the condensate feed/effluent exchanger, by preheating the process condensate going to the

process condensate stripper. The stripped condensate is finally cooled to 45°C before it is sent to the demineralization unit outside the battery limit.

A separator, B 3202, is placed at the outlet of the process condensate stripper in order to avoid carry over to the pre reformer.
