



# **Stamicarbon dual pressure nitric acid technology with high energy recovery**

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*Building on its long history in ANNA industry, Stamicarbon is introducing its dual pressure nitric acid process. The dual pressure nitric acid technology of Stamicarbon is designed to guarantee high energy recovery. This is achieved by a proper selection of the heat exchangers position downstream the ammonia burner. The main feature of the process is the high tail gas temperature, up to 480°C. This is accomplished by locating the last tail gas heater close to the Pt/Rh gauzes in the ammonia burner vessel where higher process temperatures are encountered.*

*The high tail gas temperature has several advantages. On the one hand, the N<sub>2</sub>O decomposition can be performed in a tertiary abatement system without the addition of an external reducing agent like natural gas. On the other hand, more power can be generated by the expansion turbine, decreasing the amount of work to be realised by the steam turbine. Besides this, the expanded tail gas still contains valuable heat that can be exchanged in a tail gas/tail gas heat exchanger, allowing a lower temperature in the stack and therefore, more heat recovery in the system. All these advantages are translated into higher steam export and therefore, more energy recovery.*

*A thoughtful heat exchangers distribution also allows to minimise the well-known condensation/re-evaporation effect and hence, corrosion. This allows the use of common materials of construction which reduce the manufacturing cost of the heat exchangers considerably.*

## **INTRODUCTION**

Stamicarbon has been an active licensor in the nitric acid sector, developing its own technology and building more than 40 plants between the 1950's and the 1980's. Although nitric acid licensing activities were stopped in the past, Stamicarbon recently has revived its technology and is ready to relaunch it again to the market.

Nowadays, around 20 nitric acid plants around the globe are running with Stamicarbon technology. Among them, one of the plants located at the Chemelot site (The Netherlands) has been selected as reference plant.

At this chemical site, OCI Nitrogen owns three nitric acid plants, all designed with Stamicarbon technology. The reference plant, commissioned in 1989, is designed with dual pressure technology and has a capacity of 1600 MTPD. With a very stable operation since start-up and only minor adjustments through the years, Stamicarbon's reference plant shows a competitive design, which with some additional improvements, is ready to re-enter the market.

A dual-pressure configuration allows the combination of medium oxidation pressure with high absorption pressure. The oxidation section operates at 5 bar(a) whilst the absorption section runs at a pressure of about 11 bar(a).

Typically, the dual-pressure process is used for capacities between 600 and 1600 MTPD. Larger capacities are also possible; however, some equipment, like the NH<sub>3</sub> burner, has to be double installed due to size limitations.

## STAMICARBON'S DUAL PRESSURE NITRIC ACID PROCESS DESCRIPTION

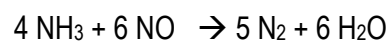
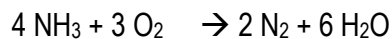
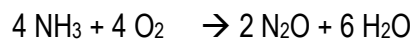
The air required for the ammonia combustion is compressed by the air compressor to ca. 5 bar(a). Prior to entering the air compressor, the air can be preheated to avoid condensation and icing and is filtered in a set of bag filters.

The compressed air is primary used for the catalytic combustion of ammonia. A small part of this compressed air is used in the bleaching column to remove dissolved NO<sub>x</sub> components from the final product.

Ammonia is received from battery limits in liquid state and is evaporated by means of cooling water. Ammonia then is superheated by means of LP steam and filtered. To get rid of the water traces in the ammonia and avoid accumulation of water in the main ammonia evaporator, a small auxiliary evaporator is operated in parallel to the main one.

Subsequently, air and NH<sub>3</sub> are mixed in a static mixer and sent to the ammonia burner. The control of ammonia content in the mixture is essential since an explosive mixture can be formed. With a maximum of 11 vol% NH<sub>3</sub> in the mixture, the explosion risks are avoided.

In the ammonia burner, NH<sub>3</sub> is oxidised to NO on Pt/Rh gauzes where also small amounts of N<sub>2</sub> and N<sub>2</sub>O are formed as side products:

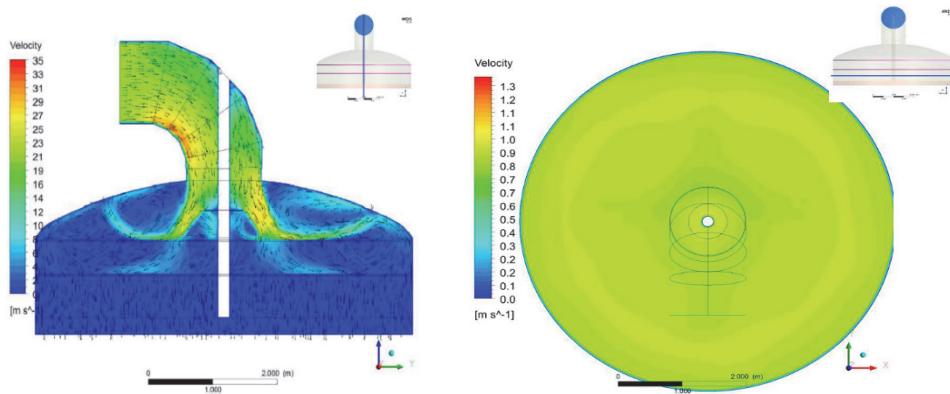


The Pt/Rh catalyst consist of several knitted gauzes formed from wire containing around 90-95% of platinum alloyed with rhodium that provides greater strength. Some of the platinum and rhodium vaporises during the reaction process and therefore, platinum recovery system is installed below the catalyst. In this system, palladium alloy, so-called "getter", is able to catch 60-80% of the total Pt losses.

The highly exothermic reaction that takes place between ammonia and oxygen maintains the required temperature on the gauzes, which is controlled at approximately 885°C. This temperature is selected as it combines an optimal ammonia conversion with low Pt losses, which are greater at higher temperatures due to some volatilisation of the metal.

Homogenous distribution of the NH<sub>3</sub>/air mixture over the Pt-gauzes is essential to guarantee optimum operation. This might be challenging especially for large nitric acid plants when the size of the ammonia burner reaches a diameter of 6 m. The distribution system becomes crucial to achieve proper operation of the gauzes. A design with perforated plates that combines a uniform gas distribution with low pressure drop is applied in the Stamicarbon process. Furthermore, this type of distribution system notably reduces the risk of pre-ignition when compared with other types of distributors like deflector plates with more dead zones where catalyst dust can settle after a back-flow scenario.

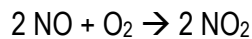
CFD studies are useful to analyse the design of the distribution plates and observe whether a proper spreading is achieved. The results from CFD studies performed by Stamicarbon are shown in figure 1. The velocity profiles show a homogenous distribution of gas over the gauzes.



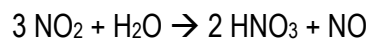
**Fig. 1: CFD velocity profile in burner head and gauzes**

The heat released by the exothermic oxidation reaction is first used to superheat the produced high pressure steam and to heat the tail gas up to 480°C in the NH<sub>3</sub> burner vessel. Subsequently, the hot gas is used to preheat boiler feed water and produce high pressure steam in the so-called waste heat boiler.

As the temperature of the process gets lower, the produced NO starts to oxidise to NO<sub>2</sub> by the following exothermic reaction:



Downstream the waste heat boiler, the nitrous gas is further cooled down in a gas/gas heat exchanger to ca. 160°C before entering the low-pressure cooler condenser. In the low-pressure cooler condenser, nitrous gas cools down below the dew point of the vapour by means of cooling water. Here, NO<sub>2</sub> is absorbed in the condensed water formed during the ammonia oxidation and a weak acid solution is produced based on the next absorption reaction:



This weak acid with a concentration of about 38 wt% is sent by a pump to the proper tray of the absorption column.

The non-condensed nitrous gas is sent to a special separator designed to efficiently remove the acid mist droplets in order to prevent corrosion in the NO<sub>x</sub> compressor. Next, the gas is compressed to 11 bar(a) by the NO<sub>x</sub> compressor and is afterwards cooled down by means of a BFW preheater.

The last cooling step takes place in the high-pressure cooler condenser where again the vapour is cooled down below its dew point and an acid solution is formed at ca. 50°C. Here, a stronger acid solution is condensed (approx. 60 wt%) and is sent by gravity to the bottom of the oxidation/absorption column.

The remaining gas enters at the bottom of the oxidation/absorption column which consists of a series of sieve trays. On the trays, NO<sub>2</sub> is absorbed in water which is introduced at the top of the column; while NO is oxidised to NO<sub>2</sub> in the free space between trays according to the reactions indicated before.

To promote the absorption and oxidation reactions, the heat released by the absorption and oxidation reactions is removed by cooling water coils mounted on the trays. Thus, along the column, the NO<sub>x</sub> content in the gas phase moving upwards, decreases from bottom to top, while the acid concentration of the liquid moving downwards, increases from top to bottom.

At the bottom of the oxidation/absorption column, the acid from the trays is mixed with the acid from the high-pressure cooler condenser and the mixed acid solution is sent to the last purification step, the bleaching.

In the bleaching column, NO<sub>x</sub> components dissolved in the solution are eliminated by means of secondary air. The secondary air is cooled down before entering the bleaching column and the heat is used to preheat boiler feed water. After passing through the bleaching column, the secondary air is injected in the suction line of the NO<sub>x</sub> compressor to provide the required O<sub>2</sub> for the oxidation of NO. The bleached nitric acid solution is sent to the storage tank.

At the top of the oxidation/absorption column, the so-called tail gas stream containing N<sub>2</sub> with traces of NO<sub>x</sub>, N<sub>2</sub>O and O<sub>2</sub> is heated in three steps. First, in a tail gas/tail gas heat exchanger; secondly, in a process gas/tail gas heat exchanger and finally, in a process gas/tail gas heat exchanger to 480°C.

In the next step of the process traces of  $\text{NO}_x$  and  $\text{N}_2\text{O}$  are eliminated before sending the tail gas to the atmosphere. A tertiary abatement system is used where  $\text{N}_2\text{O}$  and  $\text{NO}_x$  are catalytically decomposed. Since high temperature is required for the decomposition of  $\text{N}_2\text{O}$ , the reactor is located after the last tail gas heater where the temperature reaches appropriate levels. The concentration of these two components at the outlet of the abatement system can be decreased to less than 20 ppm(v) if required.

The tail gas is expanded in the expansion turbine where the in-line compressor train configuration allows the usage of the released power to drive the air and  $\text{NO}_x$  compressor. Additional power needed in the compressor train is provided by a steam turbine.

After expansion, the heat content of the tail gas stream is still sufficient to allow another heat exchange step. In this last heat exchanger, the expanded tail gas is cooled down to  $110^\circ\text{C}$  before being released to the atmosphere via the stack.

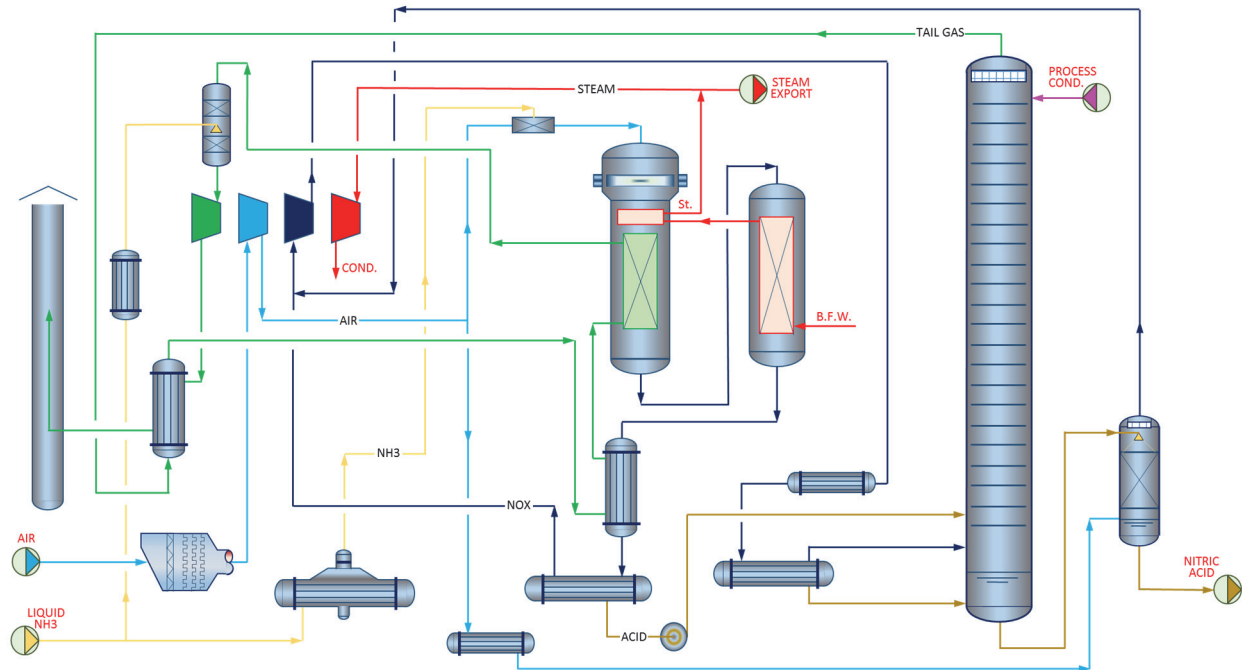


Fig. 2: Process flow diagram of Stamicarbon's dual pressure nitric acid technology

## PROCESS HIGHLIGHTS

### Corrosion prevention

When the temperature of the nitrous gas gets close to its dew point, an acid solution will condense. The acid concentration in this solution will depend on the water content in the gas and operating pressure and temperature. Once condensation has occurred, re-evaporation of water will concentrate the acid causing a severe corrosion problem. This effect is particularly detrimental in cold spots and dead zones.

In the nitric acid plants, the cooler condensers but also the preceding heat exchangers are the most prone to suffer from corrosion, especially in those areas where the temperature of the vapours gets close to the dew point.

A proper selection of process temperatures and location of the heat exchangers is key to minimise the condensation/re-evaporation effect. When the temperature of the gas stream is not sufficient to re-evaporate the acid condensed, the condensation/re-evaporation effect is minimised and the lifetime of the heat exchangers is remarkably prolonged.

Minimising the effects of the condensation/re-evaporation phenomena reduces the risk for corrosion and therefore, the use of "exotic" construction materials is avoided. As a consequence, the manufacturing cost of the heat exchangers is notably reduced.

This is demonstrated by the fact that Stamicarbon reference plant is operating for more than 30 years without main corrosion issues.

## High energy recovery

The main feature of this nitric acid process is the position of its last tail gas heater. The location of this heat exchanger in the ammonia burner vessel, below the steam superheater and before the steam boiler, allows tail gas temperatures up to 480°C. In conventional nitric acid processes, the last tail gas heater is commonly located after the steam boiler where lower process temperatures are encountered and the tail gas can be heated only to a maximum of ca. 430°C.

Stamicarbon's last tail gas heater is typically a shell and tube heat exchanger located in the same vessel as the Pt/Rh gauzes. Its location, close to the Pt/Rh gauzes, allows the use of a relatively small heat exchange area due to the fact that the available LMTD (logarithmic mean temperature difference) is larger; the driving force for heat transfer is greater and permits a smaller heat exchanger area.

Besides, as a result of its location, the outlet tail gas temperature is hardly dependent on the plant load. When the tail gas heater is located downstream the steam boiler, as in typical nitric acid production, the tail gas outlet temperature tends to be lower during low plant load which has a negative effect on the efficiency of N<sub>2</sub>O reduction when a tertiary abatement system is used.

The location of the last tail gas heater closer to the Pt/Rh gauzes has additional positive consequences in the abatement process. On the one hand, in the NO<sub>x</sub>/N<sub>2</sub>O abatement system, located downstream this heat exchanger, N<sub>2</sub>O decomposition is favoured by high temperature. It takes place without the addition of an external reducing agent like natural gas.

The next advantage is derived from the fact that higher inlet temperature to the expansion turbine allows for more power generation and hence, less power required to be supplied by the steam turbine. When comparing the power obtained in the expansion turbine by colder tail gas (430°C, as in a typical nitric acid process) and by a hotter tail gas (480°C, as in Stamicarbon's nitric acid process) with same machine efficiencies, 22 kWh/ton HNO<sub>3</sub> extra energy is obtained from the latter.

Furthermore, the expanded tail gas still contains valuable heat since its temperature is ca. 175°C. For this reason, an extra heat recovery step before releasing the tail gas to the atmosphere is feasible. For this, a tail gas/tail gas heat exchanger is used where the tail gas from the oxidation/absorption tower is heated in the tube side and the expanded tail gas from the expansion turbine is cooled in the shell side. The tail gas is released to atmosphere at 110°C versus 135°C in a typical nitric acid process and hence, more heat is recovered.

Next to relatively easy removal of NO<sub>x</sub> and N<sub>2</sub>O, these advantages are translated into higher steam export. The process allows an export of HP steam of more than 800kg steam/t HNO<sub>3</sub>, typically at a pressure of 45 bar (a) and a temperature of 450°C.

## LOW EMISSIONS

NO<sub>x</sub> and N<sub>2</sub>O are considered harmful species for the environment contributing to acid rain, greenhouse effect and ozone layer depletion.

During the manufacture of nitric acid, N<sub>2</sub>O is produced as an unwanted by-product of the catalytic oxidation of ammonia (see reactions in section 3). The different ways of lowering the emissions of N<sub>2</sub>O can be categorised in three groups:

- Primary: N<sub>2</sub>O formation is prevented. In this case, the Pt/Rh gauzes are modified to reduce the N<sub>2</sub>O production.
- Secondary: N<sub>2</sub>O is removed somewhere between the outlet of the gauzes and the absorption tower.
- Tertiary: N<sub>2</sub>O is removed downstream the absorption tower, the optimum location being the hottest position, which is upstream the expander.

A tertiary abatement system brings thus the advantage of combining both N<sub>2</sub>O and NO<sub>x</sub> depletion in one single vessel with two catalyst beds. Commercially available iron zeolite-based catalyst is used in the first catalyst bed to decompose N<sub>2</sub>O without the addition of an external reducing agent. This can only be accomplished in processes with tail gas temperature above 430°C.

The same catalyst is used in the second catalyst bed to reduce the  $\text{NO}_x$  gas to  $\text{N}_2$  and  $\text{H}_2\text{O}$ ; in this case, the addition of a reducing agent ( $\text{NH}_3$ ) is required. By means of the high temperature used in the abatement reactor (up to  $480^\circ\text{C}$ )  $\text{NH}_3$  slippage through the downstream equipment is eliminated since any excess of  $\text{NH}_3$  will be decomposed. This ensures that no ammonium nitrate is formed in the downstream equipment.

This system is designed to guarantee maximum efficiencies with lowest pressure drop and allows the catalytic reduction of  $\text{NO}_x$  and  $\text{N}_2\text{O}$  to concentrations below 20 ppm(v).

## ENERGY BENCHMARKING

Being an independent consultant, the Process Design Centre (PDC) performs global benchmarking studies on a number of (petro)chemical processes. In 2005, the PDC performed a worldwide energy benchmark on the existing nitric acid plants.

To calculate the energy consumption of each nitric acid plant, the PDC developed a method based on exergy calculation. The exergy calculation, instead of enthalpy calculation, allows for an objective comparison among plants to avoid, for instance, favouring those plants with low pressure steam export.

In this calculation, the nitric acid process is considered as a black box where only inlet and outlet streams are taken into account. From these streams, the energy carriers are identified, which are: ammonia, fuel gas, electricity, steam and hot water. The energy content of these streams is translated into exergy values. The exergy values are converted into primary fuel equivalents (PFE) by applying fixed correction factors. By dividing the primary energy over the total production of the plant, the energy efficiency in GJ/ton  $\text{HNO}_3$  is calculated.

In 2005, the PDC asked the nitric acid producers around the world to provide the required data to perform the benchmarking analysis. As a result, each producer could see how efficient their nitric acid plants were in comparison to their competitors and whether there was room for improvement.

Stamicarbon has used the same methodology to calculate the energy consumption of its process. Negative energy consumption means that the process delivers energy while positive energy values indicate that the plant needs external energy input to operate. Thus, the more negative the value, the better.

The result of this calculation indicated that Stamicarbon process delivers energy, the calculated value being  $-2$  GJ/ton  $\text{HNO}_3$ . In the benchmarking study performed in 2005, 90 plants participated and the energy consumption varied from 4 GJ/ton  $\text{HNO}_3$  (for the least efficient plant) to  $-1.8$  GJ/ton  $\text{HNO}_3$  (for the most efficient plant).

## ANNA COOPERATION

Stamicarbon current nitrogen fertiliser technology portfolio can support projects comprising an entire grass root urea ammonium nitrate (UAN) industrial complex including own urea and nitric acid technology.

In addition, for ANNA projects including the production of CAN and/or AN (FGAN, fertiliser grade AN and TGAN, technical grade AN), Stamicarbon partners with INCRO, thereby combining the nitric acid technology with an established portfolio of nitrate finishing technologies.

## CONCLUSIONS

Stamicarbon was an active nitric acid licensor in the past, building more than 40 plants all around the world. Nowadays, Stamicarbon has revived and improved its nitric acid technology and is ready to launch to the market its dual pressure nitric acid process, characterized by maximum energy recovery.

The main feature of Stamicarbon's nitric acid process is the location of the last tail gas heater. By locating it close to the Pt-Rh gauzes, high tail gas temperatures up to  $480^\circ\text{C}$  are achieved. This has several positive consequences:

- Natural gas is not required to eliminate  $\text{N}_2\text{O}$  in a tertiary abatement system
- More power is extracted from the extraction turbine
- Extra heat recovery step is allowed by adding a heater after the extraction turbine

All these advantages are translated into maximum energy recovery and therefore, higher steam export. The Stamicarbon process can guarantee steam export figures over 800 kg steam/ton  $\text{HNO}_3$ .

Besides, minimising the effects of the condensation/re-evaporation phenomena, reduces the risk of corrosion and therefore, the use of 'exotic' construction materials is avoided. As a consequence, the manufacturing cost of the heat exchangers is notably reduced. This is demonstrated by the fact that the Stamicarbon reference plant has operated for more than 30 years without major corrosion issues.

