International Fertilizer Industry Association

IFA Technical Conference

Beijing, China
20-23 April 2004

LOW N$_2$O EMISSION NITRIC ACID PROCESS

Luis M. Marzo
Espindesa, Spain

SUMMARY

N$_2$O is one of the main contributors to the greenhouse effect and to the destruction of the ozone layer. Nitric acid industry is one of the major industrial sources of N$_2$O, whose emissions will be limited in the near future.

ESPINDESA has developed an ammonia burner design which maintains the gases at high temperature for several seconds, promoting the self decomposition of N$_2$O. The burner is linked to a heat recovery system of special design, cheaper than the traditional La Mont boilers.

Several burner/heat recovery systems have been designed, one of them is in operation since 1997 in Shijiazhuang (Hebei, P.R. China).

At present, ESPINDESA is designing a 866 metric tonnes per day 68% HNO$_3$ (azeotropic acid) for the new Shanghai BASF Polyurethanes Complex in Caojing (Shanghai).

1. INTRODUCTION

Nitrous oxide (N$_2$O) has been identified as one of the 6 main compounds contributing to the greenhouse effect, next to CO$_2$ and methane. The Global Warming Potential of N$_2$O is about 310, i.e. on a 100-years time scale, N$_2$O is 310 times more effective per Kg at trapping heat in the atmosphere than CO$_2$. According to the Kyoto Protocol, nitrous oxide is one of the greenhouse gases of which the emissions have to be reduced.

In addition to the above, N$_2$O is also active in the destruction of the ozone layer.

The Nitric Acid industry is one of the major industrial sources of N$_2$O. This explains why nitric acid processors and research institutions are working in the last years in developing catalysts and techniques to reduce N$_2$O emissions in tail gas.

2. N$_2$O GENERATION

In the ammonia burner of a nitric acid plant, most of the ammonia (95-97%) is oxidized to nitrogen oxide (NO) and water using a set of gauzes of platinum-rhodium catalyst. The remainder of ammonia is either converted into nitrogen (N$_2$) or nitrous oxide (N$_2$O).

Almost all the N$_2$O produced in the ammonia burner is emitted to the atmosphere via the tail gas, because the absorption of N$_2$O in the tower is not as significant as the decomposition of N$_2$O in traditional SCR DeNOX reactors.

Typical tail gas N_2O content ranges 500-3000 ppm depending on the plant design and Pt-Rh catalyst condition. Values tend to increase when catalyst gets old (Figure 1).
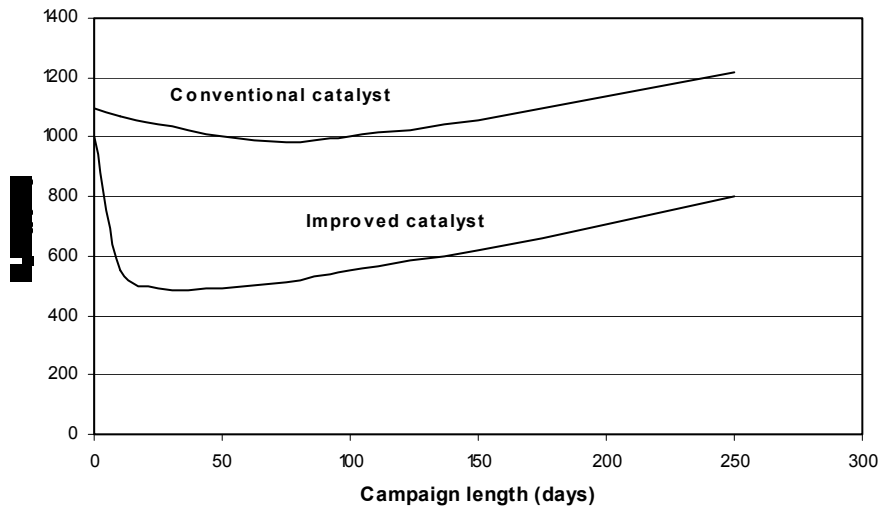

Figure 1: N_2O emissions from conventional and improved catalyst systems

Average generation for nitric acid plants ranges 3 Kg to 10 Kg of nitrous oxide per ton of 100% nitric acid.

3. N_2O ABATEMENT TECHNIQUES

Several promising techniques are currently being investigated, namely:

A) Abatement in the Ammonia Burner

- Catalyst-aided decomposition of N_2O directly after the Pt/Rh catalyst.

Catalysts developed specifically for the purpose of decomposing N_2O immediately after the Pt/Rh ammonia oxidation catalyst are in the process of being tested in nitric acid ammonia burners. Efficiencies as high as 80% have been reported. The main drawbacks are that the high temperature may affect the catalyst stability and that additionally the catalyst tends to decompose NOX too, lowering the NH_3 combustion efficiency. Also, the additional catalyst increases pressure drop and therefore increases the energy consumption of the process air compressor.

- Modification of Pt-Rh gauzes

Research work is in progress to modify the composition of the catalytic gauzes system so as to lessen the formation of N_2O. Reductions on average by more than 30% over the extended campaign lengths are claimed (Figure 1).

- Thermal decomposition by extended reactor chamber

N_2O is not stable at the elevated temperatures of ammonia burners and decomposes fairly rapidly into nitrogen and oxygen if given time; therefore ammonia burners can

be designed to enlarge the space between the platinum catalyst gauze and the heat recovery section, to provide increased residence time for hot gases at 850-900ºC.

B) Treatment of tail gas

- Direct decomposition

Catalysts are being developed for the direct decomposition of N_2O to nitrogen and oxygen, without the addition of any reductant.

By using those catalysts, the N_2O decomposition in tail gas starts at temperatures of about 300ºC. At higher temperatures the reaction rate is increased (Figure 2). For plants with a temperature of 450ºC in front of the expander, a space velocity as high as 45,000 h^{-1} can be applied to reach 70% N_2O decomposition.
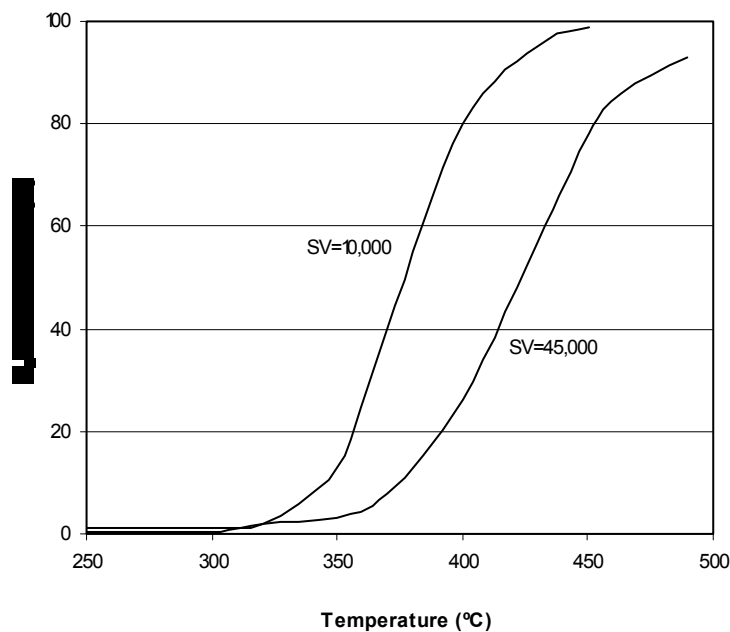

Figure 2: Direct decomposition of N_2O

At 500ºC N_2O decomposition can be higher than 95%.

As no reacting agent is added, the temperature increase due to the heat of the N_2O decomposition reaction is very limited (about 4ºC)

- Catalytic reduction

Selective and non-selective catalysts are being developed to destroy N_2O downstream the absorption column with promising results. Reductants such as hydrogen, ammonia, propane, methane, etc. are being used. High conversion ratios are being reported, although those catalysts require high ignition temperatures (200-300ºC with hydrogen up to 450-550ºC with methane). The emission of unreacted methane is unwanted, because methane is a greenhouse gas itself.

3

4. THE ESPINDESA APPROACH FOR LOW N_2O EMISSIONS

ESPINDESA has designed since the 70's, eight ammonia burners with sizes up to 3500 mm I.D. which hold the process gases for several seconds at high temperature (850-900ºC) between the catalyst gauzes and the first process gases cooler. Figure 3 shows a burner sketch of an existing plant.
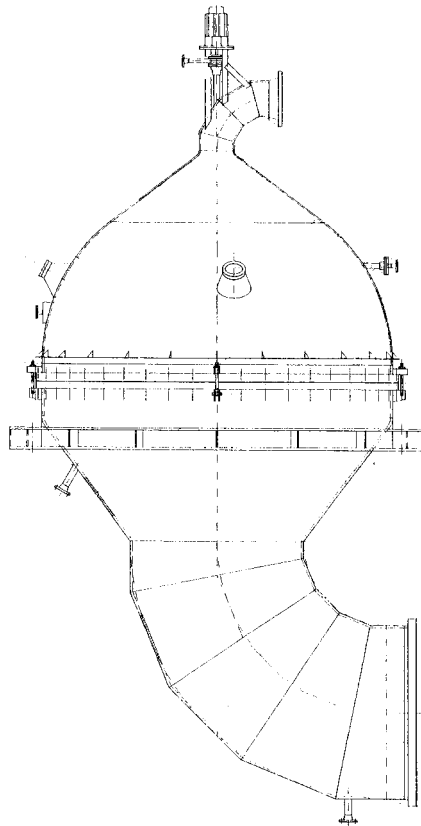

Figure 3: ESPINDESA's ammonia burner

This concept has proven to be effective in promoting the spontaneous decomposition of N_2O, provided the residence time of the gases at high temperature is sufficient.

N_2O contents in tail gas below 200 ppmv and ammonia combustion efficiencies of 95-97% are achieved.

5. ESPINDESA'S LOW N_2O NITRIC ACID PROCESS DESCRIPTION

The above concept for ammonia burners design has been applied by ESPINDESA to low⁻, medium⁻ and high⁻ pressure burners. The next description refers to the use of that concept to the design of a dual pressure nitric acid process (Figure 4).
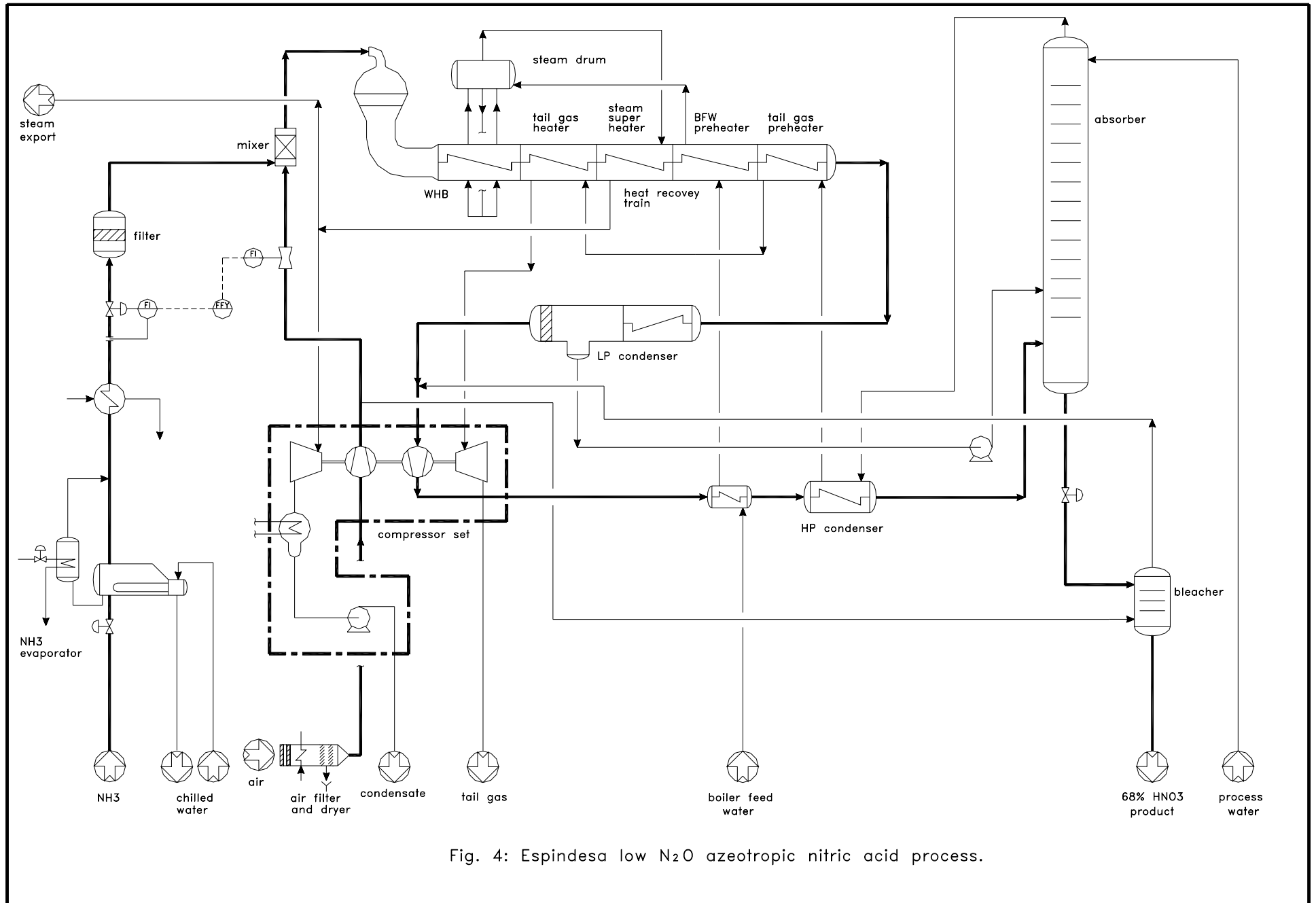
Fig. 4: Espindesa low N₂O azeotropic nitric acid process.

- Ammonia evaporation

A typical plant includes 2 ammonia evaporators:

The main one, which is of the kettle type, evaporates ammonia at 5 bars against water, which is cooled in the process and used to cool the upper trays of the absorber.

The side evaporator (coil in vessel type) also evaporates at 5 bars a mix of ammonia and water to keep low the boiling temperature in the main evaporator. The side evaporator is heated by steam.

- Ammonia oxidation

The process air is filtered and compressed at 3 bars in the first stage of the compressor set.

The evaporated ammonia is reheated, filtered and mixed with process air and enters the ammonia burner. Pt-Rh catalyst and getter gauzes system is supported over a grid of special alloys. The temperature of gases reaches 870ºC. The gases are kept during several seconds at that high temperature in a cone-shaped chamber which ends in a bend; this directs the gases into the heat exchanger train. The chamber walls and the bend are lined.

- Heat exchanger train

The heat of the gases is recovered in a series of heat exchangers where the temperature decreases from 870ºC to 145ºC. The first exchanger is a horizontal boiler designed as transfer-line exchanger. Steam at 50 bars is produced by natural draft circulation. Temperature of gases decreases from 870ºC to 500ºC.

The investment cost of the system Ammonia Burner-Hot Chamber/Bend-Horizontal boiler is considerably cheaper than the conventional La Mont type boiler design.

The rest of the exchangers which constitute the train are:

Tail gas reheater

Steam superheater

Boiler feedwater heater

Tail gas heater

The exchangers are bolted to each other and are supported on lubrite plates.

The train preheats the tail gases to turbine to 420ºC and produces and superheats all steam required by the compressor set plus an additional export of 550 Kgs of steam per ton of HNO_3.

- Dilute acid condensation

The cool gases at 145ºC enter the low pressure cooler-condenser which cools them below the dew point so most of the water produced in the ammonia oxidation reaction condenses in the form of a 35% nitric acid stream. This is separated from the gas and pumped to the appropriate tray of the absorber.

- Process gases compression and cooling

The dry process gases are mixed with the secondary air after it has been used in the bleaching tower to strip out most of the free NOX remaining in the product acid. The gases are then compressed to 12 bars.

In the ducts downstream the compressor, the NO contained in the process gas reacts with the oxygen of the secondary air and the temperature rises again to 240ºC.

Three further heat exchangers lower the temperature of the process gases down to 50ºC. The cooling media are respectively boiler feed water, tail gas and cooling water. At the end of the second cooler-condenser some drops of 70% acid are obtained and are mixed with the product acid. The dry gases enter the absorption tower.

- Absorption of NOX

At the inlet of the Absorption Tower, the oxidation of NO to NO_2 has already been completed.

The internals of the absorber are a set of sieve trays cooled with coils. The process gases flow upwards in countercurrent with water. In the space between trays NO formed during the reaction of NO_2 with water is reoxidized by oxygen to NO_2.

The number of trays depend of the tail gas NOX content permitted in the exhaust gas. Where environmental requirements are below 200 ppmv, a catalyst for DeNOX abatement may be advisable. In those cases a cost study is advised to optimize the size of the absorber.

The heat released by the absorption of NO_2 in water and by the reoxidation of NO to NO_2 is removed by the cooling coils. The upper part trays are cooled by chilled water. The lower part trays are cooled with ordinary cooling water.

The product acid leaves the bottom of the tower and is sent to the bleaching tower.

- Acid Bleaching

The acid leaving in the absorber is reddish colour owing to the presence of dissolved free NO_2. This is removed by countercurrent contact with the secondary air in a small sieve tray column. After bleaching the acid is colourless and contains less than 70 ppm HNO_2.

As mentioned, the secondary air leaving the top of the bleaching tower is laden with the nitrogen oxides, which are recycled to the process when the secondary air is united with the main process gas stream at the inlet of the second stage nitrous gas compressor.

- Tail gas treatment

The tail gas leaves the Absorption Tower at 11 bars pressure and 30ºC temperature and is reheated in three heat exchangers until 420ºC. As this point the gases enter the gas turbine which recovers about 70% of the power consumed by the air and NO compressors.

After the gas turbine the tail gas is exhausted to the atmosphere.

6. AZEOTROPIC ACID PRODUCTION

The weak nitric acid (WNA: 58-60% HNO_3) produced in a normal nitric acid process is sufficiently concentrated to be used directly in nitrate fertilizer production. But various procedures in the chemical industry require acid of concentration close to azeotropic (68% HNO_3).

To produce azeotropic acid in an ordinary nitric acid plant, two conditions must be fulfilled:

  a)   The NOX partial pressure in gases at the inlet of the absorption tower is to be close to 1 bar.

  b)   The water balance must be carefully controlled.

The first condition is fulfilled fairly easily by ensuring that the NO is fully oxidized to NO_2 and by performing the absorption under a sufficiently high total pressure to bring the NOX partial pressure close to 1 bar.

The water balance is rather more critical: In any nitric acid process water appears in three ways:

A considerable amount of water is produced in the ammonia oxidation.

Water has to be supplied to the top of the absorption tower.

A significant amount of moisture may be drawn in with the process air, especially in locations of high ambient air temperature and humidity.

Obviously there is no way of varying the amount of water produced in the ammonia oxidation. If that were the only source of water in the plant, the maximum concentration of acid that could be produced would be only about 77% HNO_3.

In practice, though, a certain minimum amount of water is needed in the top of the absorption tower, to ensure the hydraulic stability of the trays, which further reduces the attainable product concentration. That means that the only component of the total water input that can be eliminated without adverse effect is the moisture in the process air.

ESPINDESA dries the process air by cooling it with chilled water at the suction of the air compressor. Not only does this exclude extraneous moisture from the plant; it also improves the efficiency of the air compressor because water vapour is excluded and the cool air is denser than the ambient air.

7. CONSUMPTIONS

The following summarizes the main specific consumption per ton of azeotropic acid (basis 100% HNO_3) for a 1000 Tpd Plant which exhausts tail gas to the atmosphere containing 200 ppmv NOX and 200 ppmv N_2O.

-       Ammonia   281   Kgs

-       Catalyst (net) 40   mgrs

-       Steam export 550   Kgs

-       Electric power 10   10 kW