


## COMBINED CATALYTIC REMOVAL OF N<sub>2</sub>O AND NO<sub>x</sub> FROM THE TAIL GASES OF A NITRIC ACID PLANT

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## Abstract

Nitrous oxide (N<sub>2</sub>O) is greenhouse gas with a high global warming potential. The nitric acid industry is a major source of N<sub>2</sub>O. ECN developed a technique for the catalytic removal of N<sub>2</sub>O from the tail gases of a nitric acid plants. The most cost effective method for N<sub>2</sub>O abatement is direct decomposition (0.3 to 1 EUR/ton CO<sub>2</sub> equivalents removed). However, this technique can only be used when the tail gas temperature is higher than 400°C. Selective catalytic reduction (SCR) of N<sub>2</sub>O with LPG can be used in plants with a tail gas temperature below 400°C. The use of a reductant makes this method more expensive; the cost is 1.3 to 2 EUR/ton CO<sub>2</sub> equivalents removed. Combination of N<sub>2</sub>O removal with the destruction of NO<sub>x</sub> in a single reactor is an opportunity to improve the overall cost effectiveness.

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## 1. INTRODUCTION

Nitrous oxide ( $N_2O$ ) is a potent greenhouse gas (it has a 310 times larger impact on global warming than  $CO_2$ ), and is one of the targeted molecules in the Kyoto protocol. Nitrogen oxides ( $NO_x$ ) are amongst others responsible for acid rain, entroplication, photo-chemical air pollution and stratospheric ozone depletion. Nitric acid plants emit relatively high concentrations of both compounds. The  $NO_x$  emissions of many nitric acid plants are still untreated and for  $N_2O$  removal no proven commercial technologies are available yet.

The current technology for  $DeNO_x$  in applications such as nitric acid plants is selective catalytic reduction (SCR) using ammonia as a reductant and in many cases vanadium-pentoxide-type catalysts. Unfortunately, this process does not work for removal of  $N_2O$ .

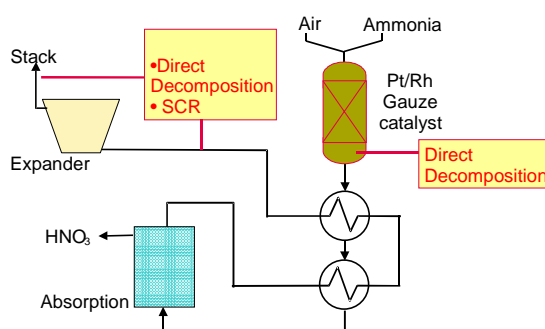


Figure 1.1 Possible locations for  $N_2O$  removal in a nitric acid plant

Stimulated by the Kyoto protocol, several initiatives are being developed for  $N_2O$  destruction in nitric acid plants. R&D focuses on two locations for  $N_2O$  removal: directly behind the ammonia oxidation catalyst and in the tail gases. The first technique – catalytic decomposition of  $N_2O$  at high temperature – would for many plants offer a simple and cost effective way to remove  $N_2O$ . However, possible drawbacks are that catalyst life may be short due to the high temperature and that the decomposition of  $NO$  is catalysed. This would cause production losses and consequently influence the cost efficiency dramatically. Destruction of nitrous oxide behind the absorption section, in the tail gases of the nitric acid plant – where the conditions are less severe and  $NO_x$  decomposition is not a problem – may be a safer option.

ECN developed a catalytic system for  $N_2O$  removal from the tail gases of a nitric acid plant. Both upstream the expander (where the temperature is 250 - 500°C and pressure is 4 to 12 bara) and downstream the expander (atmospheric pressure, temperature 100 to 200°C) are considered possible locations.

In the literature, many materials have been screened for the direct decomposition of nitrous oxide [1]. Temperatures for complete conversion of  $N_2O$  of as low as 250°C have been reported [2]. However, these tests have not been performed under conditions that are relevant for the nitric acid industry. Especially the presence of water in the off gases inhibits the destruction of  $N_2O$  at low temperatures.

To date, no catalyst has been found that shows sufficient  $N_2O$  destruction efficiency below 400°C in presence of water. However, in many of the nitric acid plants in Europe the temperature behind the absorption section is lower than 400°C.

Destruction of  $N_2O$  can be carried out at lower temperature by adding a reductant. ECN developed an iron-containing zeolite catalyst for the selective catalytic reduction of  $N_2O$  using hydrocarbons as a reductant [3]. The catalyst did not deactivate in a 2000-hour test under demanding conditions (450°C, 6%  $H_2O$ ). Hydrocarbons such as propane (or LPG) and methane (widely available as natural gas) are used as the reducing agent.

In this paper lab tests of the catalyst in direct decomposition and selective catalytic reduction of  $N_2O$  are described. The results have been used for a technical and economic evaluation. Based on the catalyst for SCR of  $N_2O$ , ECN developed a system for combined removal of both  $N_2O$  and  $NO_x$ . The system is contained in one reactor and requires a single injection of hydrocarbons.

## 2. BASIS OF DESIGN

For the catalytic tests and the calculation of the cost efficiency, the following gas composition was used, which is representative for nitric acid plants in the Netherlands.

Table 2.1 *Gas composition*

<i>Gas</i>	<i>Concentration</i>
N <sub>2</sub> O	1500 ppmv
NO	100 - 500 ppmv
NO <sub>2</sub>	0 - 100 ppmv
O <sub>2</sub>	2.5 vol.%
H <sub>2</sub> O	0.5% vol.%
N <sub>2</sub>	balance

The calculations were based on a plant with the following characteristics (Table 2.2). Calculations of the investment and operating costs were performed by Jacobs Comprimo Nederland (a division of Stork Engineers and Contractors B.V.) according to the Netherlands Environmental Ministry's guidelines [4]. The influence of the variation of several parameters – such as the tail gas temperature, price of the reducing agent, price of the catalyst – was assessed to make the calculated cost efficiencies valid for a range of plants.

Table 2.2 *Typical plant characteristics*

<i>Characteristic</i>	<i>Value</i>
HNO <sub>3</sub> capacity	600 kton/year
N <sub>2</sub> O emission	5 kton/ year
CO <sub>2</sub> equivalents	1.5 Mton/year
Tail Gas flow	200,000 Nm <sup>3</sup> /h
Pressure upstream expander	10 bara
Temperature upstream expander	350°C <sup>1</sup>
Pressure downstream expander	1 bara
Temperature downstream expander	100°C

<sup>1</sup> For calculations of the cost efficiency of direct decomposition of N<sub>2</sub>O a tail gas temperature of 450°C was assumed.





### 3. RESULTS OF THE CATALYTIC TESTS

#### 3.1 N<sub>2</sub>O destruction in front of expander

In general, higher pressures and temperatures in the tail gas upstream the expander of nitric acid plant favour N<sub>2</sub>O destruction. Three options were investigated:

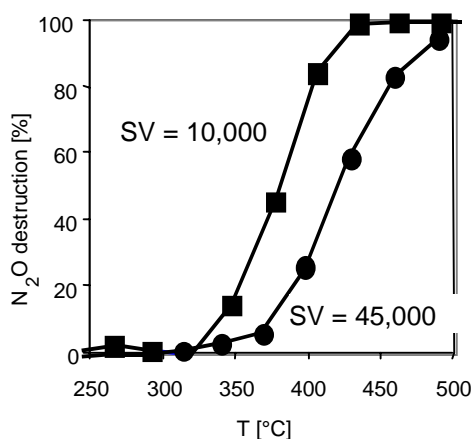


Figure 3.1 *Direct decomposition of N<sub>2</sub>O. Conditions: p = 4 bara, 1500 ppmv N<sub>2</sub>O, 200 ppmv NO<sub>x</sub>, 0.5% H<sub>2</sub>O, 2.5% O<sub>2</sub>*

- Direct decomposition on the ECN Fe-zeolite is possible from off gas temperatures of around 400°C: 80% N<sub>2</sub>O conversion at a space velocity of 10,000 h<sup>-1</sup> (STP) was achieved. At higher temperatures N<sub>2</sub>O conversion is higher and/or a lower catalyst volume can be used. At 450°C, a space velocity of 45,000 h<sup>-1</sup> can be applied to reach 80% N<sub>2</sub>O conversion.
- At much lower temperature, selective catalytic reduction of nitrous oxide using propane as a reductant is possible on the same catalyst. At a reactor inlet temperature as low as 275°C, 80% N<sub>2</sub>O destruction efficiency is possible at a space velocity of 20,000 h<sup>-1</sup> (see Figure 3.2). The propane/N<sub>2</sub>O ratio used is 1:1. A slightly modified catalyst has the same high N<sub>2</sub>O destruction efficiency and a below 10 ppmv CO formation.
- Methane could be used as an alternative reducing agent. At around 350°C 80% N<sub>2</sub>O reduction takes place at a space velocity of 20,000 h<sup>-1</sup>. However, the slip of unreacted methane (itself a greenhouse gas) is rather high. Methane conversion is expected to be satisfactory at pressures at which dual-pressure type nitric acid plants are being operated (10-12 bara).

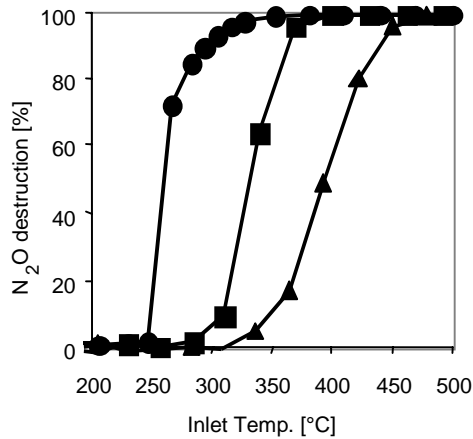


Figure 3.2  $N_2O$  destruction.

- : SCR with propane
  - : SCR with methane
  - ▲: direct decomposition
- $p = 4 \text{ bara}$ ,  $S.V. = 20,000 \text{ h}^{-1}$ ,  $1500 \text{ ppmv}$   
 $N_2O$ ,  $500 \text{ ppmv NO}$ ,  $0.5\% H_2O$ ,  $2.5\% O_2$ ,  
 (●:  $1500 \text{ ppmv C}_3H_8$ ), (■:  $4500 \text{ ppmv CH}_4$ )

The SCR of  $N_2O$  with hydrocarbons is an exothermic reaction and the adiabatic temperature rise is 30 to  $100^\circ\text{C}$ , depending on the concentration of added hydrocarbon. In an existing nitric acid plant, the expander is usually designed to work at a very well-defined temperature, so the heat of the  $\text{DeN}_2\text{O}$  reaction has to be removed. For this purpose a tail gas cooler can be used. Direct decomposition of  $N_2O$  produces only 3 to  $5^\circ\text{C}$  of heat; cooling of the gases before they enter the expander is normally not necessary.

### 3.2 $N_2O$ destruction downstream the expander

At atmospheric pressure and temperatures of  $100\text{--}200^\circ\text{C}$  both direct decomposition and SCR are not possible, unless the off gases are preheated. After start up by an additional burner, the heat generated by SCR of  $N_2O$  is used to maintain the off gases at the required temperature. Addition of  $500 \text{ ppmv}$  of propane (propane/ $N_2O = 1:3$ ) is sufficient. At atmospheric pressure and a space velocity of  $20,000 \text{ h}^{-1}$ ,  $80\%$   $N_2O$  destruction efficiency is reached at  $350^\circ\text{C}$ .

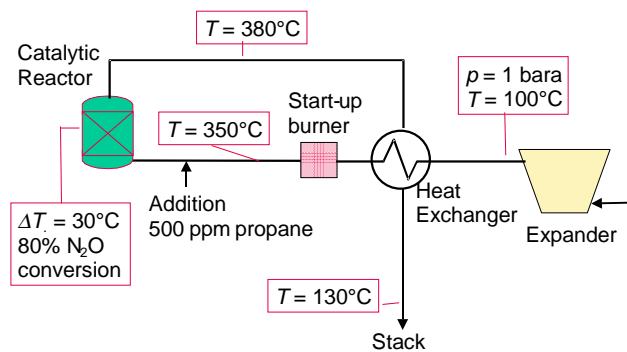


Figure 3.3 Scheme for  $N_2O$  removal facility downstream the expander

Figure 3.3 provides a schematic representation of an end-of-pipe installation for selective catalytic reduction of  $N_2O$ . Direct decomposition downstream the expander is also possible, but the off gases need to be preheated to about  $450^\circ\text{C}$  by a natural-gas-fired inline burner.

### 3.3 Combined DeNO<sub>x</sub>/DeN<sub>2</sub>O

The selective catalytic reduction of both NO<sub>x</sub> and N<sub>2</sub>O takes place when a second metal-exchanged zeolite catalyst is combined with the DeN<sub>2</sub>O catalyst. Propane was used as reductant. Destruction efficiency of both NO<sub>x</sub> and N<sub>2</sub>O is higher than 80% at a tail gas temperature above 280°C at a space velocity of 15,000 h<sup>-1</sup> for the total DeNO<sub>x</sub>/DeN<sub>2</sub>O system (see Figure 3.4). With the catalyst volume halved, NO<sub>x</sub> and N<sub>2</sub>O destruction efficiency is only slightly lower.

At atmospheric pressure conversions of NO<sub>x</sub> and N<sub>2</sub>O are somewhat lower, at a total space velocity of 15,000 h<sup>-1</sup> a temperature of 350°C results in 80% destruction of both NO<sub>x</sub> and N<sub>2</sub>O.

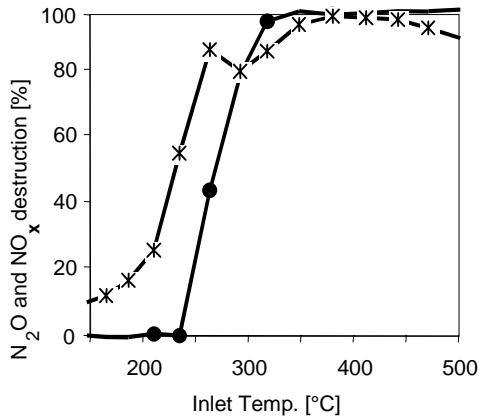


Figure 3.4 SCR of N<sub>2</sub>O and NO<sub>x</sub>,  $p = 4 \text{ bara}$ ,  $S.V. = 15,000 \text{ h}^{-1}$ , 1500 ppmv N<sub>2</sub>O, 500 ppmv NO, 1500 ppmv C<sub>3</sub>H<sub>8</sub>, 2.5 vol.% O<sub>2</sub>, 0.5 vol.% H<sub>2</sub>O



## 4. TECHNICAL AND ECONOMIC EVALUATION<sup>f</sup>

The calculations of the cost efficiency are based on retrofit of a DeN<sub>2</sub>O facility in an existing plant. So for DeN<sub>2</sub>O upstream the expander, costs as those for a tail gas cooler to remove the heat of the DeN<sub>2</sub>O reaction before entering the expander, are included. Also a retrofit factor – which accounts for extra costs due to changes in the plant – of 50 to 200% of the total investment costs was used. Losses in the energy recovery caused by pressure drop upstream or downstream the expander are also taken into account. Pressure drop over the catalytic reactor is typically 20 to 40 mbar. The use of heat exchangers in the case of SCR adds another 80 to 100 mbar. In the case of SCR upstream the expander, the revenues for the steam produced in the tail gas cooler have been taken into account.

In Table 4.1 examples of the calculation of the investment costs, annual costs and the cost efficiency are shown.

Table 4.1 Exploitation costs and cost efficiency (base cases)

Post	Unit	Direct Decomposition <sup>1</sup>	SCR Upstream expander <sup>2</sup>	SCR downstream expander <sup>3</sup>
Investment Costs	10 <sup>6</sup> EUR	2.5	4.5	5.1
<i>Exploitation Cost</i>				
Capital Cost	10 <sup>3</sup> EUR/year	341	622	724
Fixed Operation	10 <sup>3</sup> EUR/year	126	265	294
Energy <sup>4</sup>	10 <sup>3</sup> EUR/year	-	2,297	603
Recovery Losses	10 <sup>3</sup> EUR/year	90	453	272
Steam Revenues	10 <sup>3</sup> EUR/year	-	526	-
<i>Annual Cost</i>	10 <sup>3</sup> EUR/year	557	3,111	1,893
Efficiency N <sub>2</sub> O	%	70	90	90
Reduction N <sub>2</sub> O	ton/year	3,248	4,183	4,183
Cost per ton N <sub>2</sub> O	EUR/ton N <sub>2</sub> O	171	704	416
CO <sub>2</sub> equivalents	10 <sup>3</sup> ton/year <sup>1</sup>	1,006	1,282	1,285
Cost per ton CO <sub>2</sub>	EUR/ton CO <sub>2</sub>	0.5	2.3	1.5

<sup>1</sup> Direct decomposition upstream expander. Tail gas temperature = 450°C; Space velocity = 45,000 h<sup>-1</sup>; N<sub>2</sub>O conversion = 70%; Retrofit factor = 50%.

<sup>2</sup> SCR of N<sub>2</sub>O upstream the expander using 1900 ppmv propane. Tail gas temperature = 350°C; Space velocity = 20,000 h<sup>-1</sup>; N<sub>2</sub>O conversion = 90%; Retrofit factor = 50%.

<sup>3</sup> End-of-pipe SCR of N<sub>2</sub>O using 500 ppmv of propane. Tail gas temperature = 100°C; Space velocity = 20,000 h<sup>-1</sup>; N<sub>2</sub>O conversion = 70%; No retrofit factor.

<sup>4</sup> Includes the costs of LPG a reducing agent at 0.35 EUR/kg, which includes transportation costs.

The costs per ton CO<sub>2</sub> equivalents removed for direct decomposition are about 4 times lower than those for SCR. The main cause is the high costs associated with the reducing agent in the case of SCR (30 - 70% of the total annual costs).

<sup>f</sup> Calculations have been performed by Jacobs Comprimo Nederland, a division of Stork Engineers & Contractors B.V. (see ref. 4).

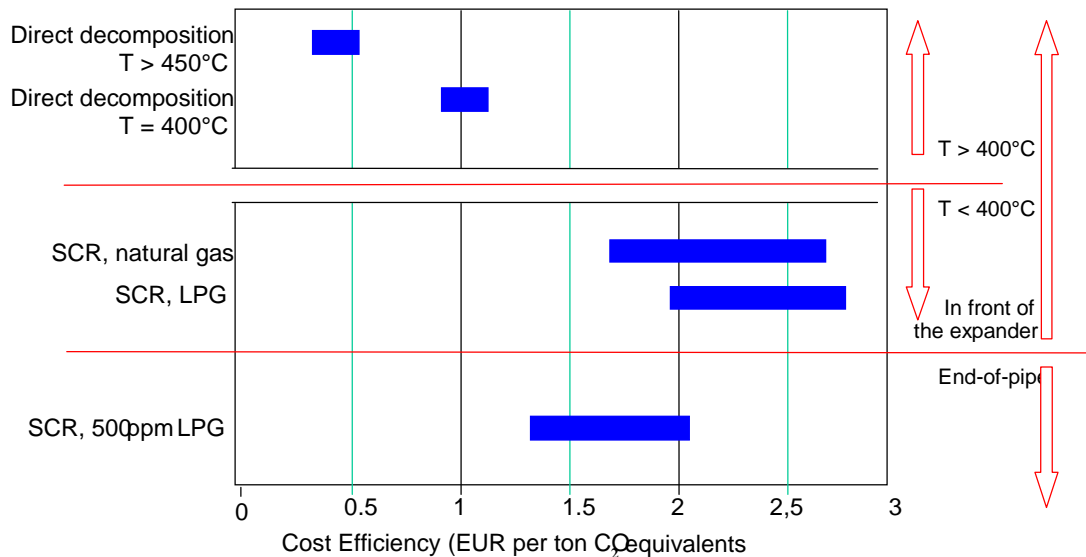


Figure 4.1 Comparison of cost efficiency of the various options for  $N_2O$  removal in a nitric acid plant

The cost efficiency values in Table 4.1 refer to a specific case, as described in the footnotes of the table. Many factors influence the cost efficiency. In the case of De $N_2O$  upstream the expander, the complexity for process integration plays an important role. For SCR of  $N_2O$ , the consumption and the price of the reducing agent (propane/LPG) have a major influence on the annual costs. Also the  $N_2O$  removal efficiency is an important factor. For example, in the case of direct decomposition the costs per ton  $CO_2$  equivalents removed are lower when a lower space velocity (i.e. larger reactor, higher catalyst volume) is applied. The higher investment costs are more than counterbalanced by the larger amount of  $CO_2$  equivalents removed.

Many parameters have been varied, which amounts to a certain range in which the costs of a De $N_2O$  technique vary. These ranges have been given in Figure 4.1.

## 5. CONCLUSIONS

For an existing nitric acid plant, direct catalytic decomposition is an economic option for N<sub>2</sub>O reduction. With the ECN catalyst 70% N<sub>2</sub>O conversion can be reached at 400°C with a space velocity of 13,000 h<sup>-1</sup>. At higher temperatures conversion increases and lower space velocities (less catalyst) can be used, which strongly improves the cost efficiency. The costs per ton CO<sub>2</sub> equivalents range from 0.4 to 1 EUR.

When the temperature in front of the expander is lower than 400°C, selective catalytic reduction of N<sub>2</sub>O is an alternative. This technique can in principle be used in any nitric acid plant, either upstream or downstream the expander. High removal efficiencies can be reached and emission of by-products (e.g. CO) is below 10 ppmv. Removal of N<sub>2</sub>O by SCR requires the use of a reductant (natural gas or LPG), costs of which contribute importantly to the total costs (20 to 60%). The costs per ton CO<sub>2</sub> equivalents removed vary between 1.3 and 3 EUR.

Based on the SCR technique for N<sub>2</sub>O, ECN also developed a system for simultaneous destruction of N<sub>2</sub>O and NO<sub>x</sub>. More than 80% removal efficiencies of both compounds is possible at tail gas temperatures of 280°C and higher.





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