

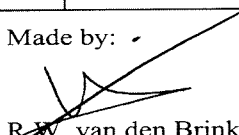


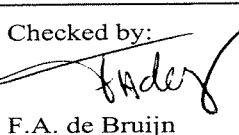

COMBINED CATALYTIC REMOVAL OF NO_x AND N₂O IN A SINGLE REACTOR FROM THE TAIL GAS OF A NITRIC ACID PLANT

Final Report

Ontwikkeling van een katalytisch systeem in een enkele reactor voor de gecombineerde verwijdering van NO_x en N₂O uit industriële afgassen in de salpeterzuurindustrie

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Revisions		
A	Draft version 09 January 2002	
B	Final Version 15 February 2002	
Made by:  R.W. van den Brink	Approved:  J. W. Erisman	ECN Clean Fossil Fuels Hydrogen Technologies & Applied Catalysis 
Checked by:  F.A. de Bruijn	Issued:  C.A.M. van der Klein	

Abstract

The nitric acid industry in the Netherlands is a major industrial source of nitrous oxide (N₂O), an important contributor to the greenhouse effect. In many nitric acid plants also the reduction of the emissions of NO_x is desirable. This project aims at developing a technique for the simultaneous removal of NO_x and N₂O by selective catalytic reduction using hydrocarbons as reductant. A system comprising of two catalysts in a single reactor has been tested under conditions representative for a Dutch nitric acid plant (1500 ppmv N₂O, 500 ppmv NO, 0.5 vol.% H₂O, 2.5 vol.% O₂). Both at atmospheric and high pressure (10 bar(a)) about 90% removal efficiency of NO_x and N₂O was achieved at 350°C when 1000 ppmv of propane was added. The cost efficiency of the atmospheric as well as the high-pressure set-up are about equal to the reference case (separate conventional NH₃-DeNO_x and propane-DeN₂O): about 2 € per ton CO₂ equivalents or 1.8 € per kg NO_x.

Keywords

Nitrous oxide, N₂O, NO_x, nitric oxides, greenhouse effect, nitric acid production.

Samenvatting

De salpeterzuurindustrie is een substantiële Nederlandse industriële bron van lachgas (N₂O), een belangrijk broeikasgas. In veel salpeterzuurfabrieken is ook verlaging van de NO_x emissies gewenst. In dit project wordt een methode ontwikkeld om zowel NO_x als N₂O te verwijderen door middel van selectieve katalytische reductie met behulp van koolwaterstoffen. Een systeem bestaande uit twee katalysatoren in één reactor is getest onder representatieve condities voor een Nederlandse salpeterzuurfabriek (1500 ppmv N₂O, 500 ppmv NO, 0.5 vol.% H₂O, 2.5 vol.% O₂). Zowel bij atmosferische als hoge druk (10 bar(a)) is een NO_x en N₂O verwijderingsgraad van ca. 90% mogelijk bij 350°C, wanneer 1000 ppmv propaan wordt toegevoegd. De kosteneffectiviteit van zowel de atmosferische als de hoge druk variant zijn bij benadering gelijk aan de referentie (separate conventionele NH₃-DeNO_x en propaan-DeN₂O): ca. 2 € per ton CO₂ equivalenten of 1.8 € per kg NO_x.

Trefwoorden

Lachgas, N₂O, NO_x, stikstofoxiden, salpeterzuurproductie, broeikas effect.

Verantwoording

Aan dit project is in het kader van het Besluit Milieusubsidies, Regeling Milieugerichte Technologie een subsidie verleend uit het programma Reductie Luchtemissies Bedrijven 1999 dat gefinancierd wordt door het ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer. Novem beheert dit programma.

Novem-projectnummer: 358510/0810.

ECN projectnummer: 7.2450.

De begeleidingscommissie bestond uit: Dr. K. Schöffel (Norsk Hydro), Drs. W. Ch. Glasz (DSM), M. Pottier (consultant), Ir. J. Williams-Jacobse (Ministerie van VROM) en Ir. W.C. van der Lans (Novem BV).

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SUMMARY

The nitric acid industry in the Netherlands is a major industrial source of nitrous oxide (N₂O), an important contributor to the greenhouse effect. If all nitrous oxide is removed from the off gases of the Dutch nitric acid plants, about 15% of the targeted 50 Mton CO₂ equivalents emission reduction for 2010 is achieved. It is also in many cases desirable to reduce emissions of NO_x. This project aims at developing a technique for the simultaneous removal of NO_x and N₂O by selective catalytic reduction using hydrocarbons as reductant. This report describes development of the technique at laboratory scale.

The ECN catalyst for removal of N₂O is placed in series with a catalyst for NO_x removal in a single reactor. Propane is used as a reducing agent. For the atmospheric pressure case the configuration is a space velocity of 30,000 h⁻¹ through the DeNO_x catalyst and 20,000 h⁻¹ through the DeN₂O catalyst. The lowest possible input of the reducing agent propane is 1000 ppmv. Conversions of N₂O (original concentration 1500 ppmv) and NO_x (original concentration is 500 ppmv) are around 90%. At high pressure the NO_x and propane conversion is strongly increased. The downside of this effect is that the amount of propane that reaches the second catalyst for reaction with N₂O is very low. So direct decomposition is the main reaction taking place on the DeN₂O catalyst, instead of SCR. The chosen configuration is a space velocity of 120,000 h⁻¹ through the DeNO_x catalyst and 10,000 h⁻¹ through the DeN₂O catalyst. Like in the atmospheric pressure case 1000 ppmv of propane is necessary.

On the basis of these results a technical and economic evaluation has been carried out. The costs of the atmospheric and high pressure options are compared to a reference case: conventional NH₃-DeNO_x in front of the expander and propane-DeN₂O downstream the expander. The cost efficiency is given for either NO_x or N₂O: all costs are contributed to N₂O or NO_x reduction only. The other reduced component is then considered as a positive side effect.

Table S.1 *Results for conventional and combined DeNO_x and DeN₂O systems, based on 90% reduction of 500 ppmv NO_x and 90% reduction of 1500 ppmv N₂O*

Post	Unit	Reference System	Hydrocarbon assisted	
			atm. pres.	high pres.
Investment Cost	10 ⁶ €	6.9	5.6	6.2
Annual Cost	10 ⁶ €/yr	2.7	2.7	2.6
Cost efficiency				
- NO _x	€/kg	1.8	1.8	1.7
- N ₂ O	€/kg	0.6	0.6	0.6
- CO ₂ eq.	€/ton	2.1	2.1	2.0

Cost efficiencies of the three cases are about equal. The reason that the single-reactor system is not cheaper than the reference case is that the dosing of propane is high. An opportunity to lower the costs of the reducing agent is the replacement of propane with methane. A novel catalyst was synthesised and some promising results were achieved.

For the reference case the industry will prefer the two-reactor system, because of the higher flexibility and the fact that NH₃-DeNO_x is a proven technology. For specific plants, e.g. with a very low tail gas temperature or with limit space for retrofit, however, the combined DeNO_x and DeN₂O system could be preferred above the reference system.

1. INTRODUCTION

1.1 NO_x and N₂O abatement in a nitric acid plant

The nitric acid industry is one of the major industrial sources of N₂O. In the Netherlands the contribution of the nitric acid production to the total N₂O emissions is about 40%. Nitrous oxide is a by-product of the oxidation of ammonia to NO_x. Its concentration in the off-gases ranges from 500 to 3500 ppmv, with an average around 1500 ppmv [1]. Nitrous oxide is one of the greenhouse gases of which the emissions have to be reduced according to the Kyoto protocol. If all nitrous oxide is removed from the off gases of the Dutch nitric acid plants, about 15% of the targeted 50 Mton CO₂ equivalents emission reduction for 2010 is achieved.

The emission of NO_x occurs because the absorption section of a nitric acid plant – where NO_x are absorbed in water to form nitric acid – is not 100% efficient. NO_x emissions of a nitric acid plant range from 100 to 2000 ppmv, with an average of 200 to 500 ppmv [1].

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. In several nitric acid plants a DeNO_x unit has been installed recently in order to comply with emission targets. The DeNO_x unit is generally located upstream the expander in the tail gases of the plant (position 2a in Figure 1.1). Unfortunately, the conventional NH₃-DeNO_x catalysts do not reduce N₂O emissions.

Non-selective catalytic reduction (NSCR) is an end-of-pipe technique aiming at reducing all reducible compounds in the gas using hydrogen or methane. Both NO_x and N₂O are removed by this technique. The costs are high due to high input of reducing agent and the retrofitting of this technique in existing nitric acid plants is very complicated due to the high heat production [2,3]. It is not considered as a promising technique for NO_x and N₂O removal [3].

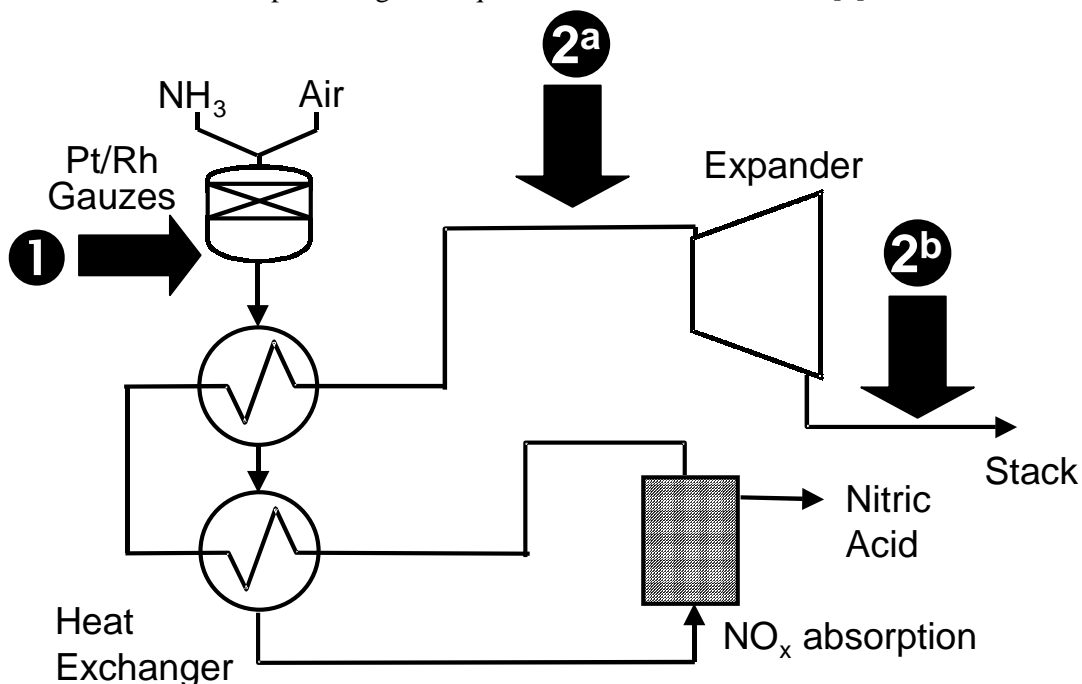


Figure 1.1 *Simplified scheme of a nitric acid plant*

Stimulated by the Kyoto protocol, several initiatives are being developed for N₂O destruction in nitric acid plants [2,3]. A promising technique for N₂O abatement in the nitric acid industry is direct catalytic decomposition. This technique can be applied either directly behind the Pt/Rh gauzes (location 1 in Figure 1.1) or in front of the expander in the tail gases (location 2a in Figure 1.1). In the first option direct decomposition occurs at high temperature. It is regarded as a cost-effective technique (0.3 - 1 € per ton CO₂ equivalents) [2,3]. A disadvantage of the technique is that it is located in front of the NO_x absorption section, which means that it may have a negative effect on the quantity and quality of the product. Next to N₂O decomposition, the catalyst could also promote destruction of NO. Wear of the catalyst can introduce metallic impurities (metal nitrates) in the ammonium nitrate, which may induce safety hazards. All these effects are currently being investigated in full-scale field tests by BASF and Norsk Hydro.

Catalytic decomposition of nitrous oxide behind the absorption section, in the tail gases of the nitric acid plant, has a relatively limited influence on the nitric acid production process. The cost efficiency is estimated at 0.5 to 1 € per ton CO₂ equivalents [2]. A major disadvantage is that application is only possible in plants with a temperature higher than 400°C in front of the expander. This problem is not relevant for the Dutch nitric acid plants, because all six have a tail gas temperature of 400°C or higher.

ECN developed a technique for N₂O abatement based on selective catalytic reduction (SCR) using a hydrocarbon as a reducing agent [4]. This technique is located in the tail gases of a nitric acid plant, either in front of or behind the expander (locations 2a or 2b in Figure 1.1). Compared to direct decomposition, the annual costs of the SCR technique are rather high. This is caused by the relatively high amounts of the expensive reducing agent necessary. The resulting cost efficiency is 1.5 to 3 € per ton CO₂ equivalents.

For a more elaborate discussion of the different options for N₂O abatement, see reference [3].

ECN embarked on a study of the possibility to combine N₂O and NO_x reduction in a single reactor using hydrocarbons as reducing agents. We expect that this can improve cost efficiency compared to two separate systems for N₂O and NO_x destruction.

2. PROJECT OVERVIEW

2.1 Aim of the project

The project aims at combining the ECN DeN₂O catalyst and a DeNO_x catalyst in a single reactor for the SCR of N₂O and NO_x. For the major part of the project propane is used as the reducing agent. For the use of methane as a reducing agent, the project aims at the application of a novel methane-DeNO_x catalyst. To this end the catalyst is tested in a simulated off gas of a nitric acid plant. We aim at the highest possible N₂O and NO_x destruction efficiencies at the lowest possible costs.

2.2 Project set-up

The first step of the project was the selection of a catalyst for NO_x removal using propane as a reducing agent under simulated conditions of a nitric acid plant. This catalyst was combined with the ECN Fe-ZSM5 DeN₂O catalyst [5]. Subsequently, the best configuration of the two catalysts and the necessary amount of added propane was determined for the atmospheric and high-pressure options. The catalytic tests were performed by ECN. Chapter 3 summarises the most important results. A detailed account of the catalytic tests is given in the progress reports [6, 7, 8].

The extrapolation of the results at 4 bar(a), which was the highest pressure possible on the ECN catalyst test bench, to 10 bar(a) proved not to be straightforward. To be able to predict the NO_x and N₂O conversions at 10 bar(a) a kinetic model of the catalytic reactor was designed (Chapter 4). To verify the model some tests at 10 bar(a) were performed. Finally, methane was studied as a cost-effective alternative for the use of propane as a reducing agent (Chapter 3). The development of a new catalyst was carried out in co-operation with an ECN project aimed at development of a methane-DeNO_x catalyst for small-scale energy generation.

Parallel to the catalytic tests, a technical and economic evaluation was being performed by Emission Care. The cost calculations used the outcome of the experiments as input. The outcomes of the cost calculations subsequently influenced the direction of the catalytic research. The result of the technical and economic evaluation is a comparison of the costs of the atmospheric and the high-pressure option with a reference case (Chapter 5).

3. CATALYST TESTS

3.1 Conditions

The tests of the catalyst were performed by ECN using a fully automated flow set-up. The set-up allows tests under simulated nitric acid plant tail gas conditions and can be operated under pressure. Table 1 summarises the test conditions.

Table 3.1 *Reaction conditions*

Conditions	
Pressure range	1 to 4 bar(a)
Temperature range	150 - 500°C
Reactor diameter	25 mm
Catalyst particles	0.71 - 1.4 mm
Standard Gas composition	
N ₂ O	1500 ppm
NO	500 ppm
NO ₂	-
H ₂ O	0.5 vol.%
O ₂	2.5 vol.%

The composition of the tail gas is different for every nitric acid plant. In agreement with Hydro Agri and DSM a representative gas composition was established, which was used in the tests. The NO_x concentration has been set at 500 ppmv. This is rather high for the nitric acid plants in the Netherlands, where NO_x emissions are in the range of 200 ppmv. The influence of variations in the concentration of several compounds was also investigated.

3.2 Concept of the catalytic system

The Fe-zeolite catalyst previously used for N₂O destruction is also active in NO_x removal [5,6]. However, at the temperature where N₂O reduction is high (reactor inlet temperatures higher than 300°C), the conversion of NO_x starts to decrease (see Figure 3.1). With this catalyst simultaneous removal of N₂O and NO_x is not possible.

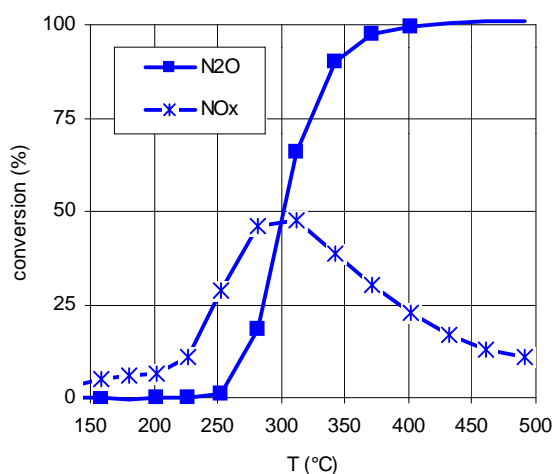


Figure 3.1 *NO_x and N₂O conversion vs. catalyst inlet temperature on the ECN Fe-zeolite catalyst. Conditions: p = 1 bar(a), S.V. = 30,000 h⁻¹, 1500 ppmv N₂O, 500 ppmv NO, 2.5 vol.% O₂, 0.5 vol.% H₂O, 1500 ppmv C₃H₈, balance N₂.*

The catalytic system used in this project is a combination of the iron-containing zeolite catalyst and a cobalt-containing zeolite catalyst. The latter is a known catalyst for the removal of NO_x with hydrocarbons as a reducing agent. Figure 3.2 shows schematically the concept of the two catalysts placed in series.

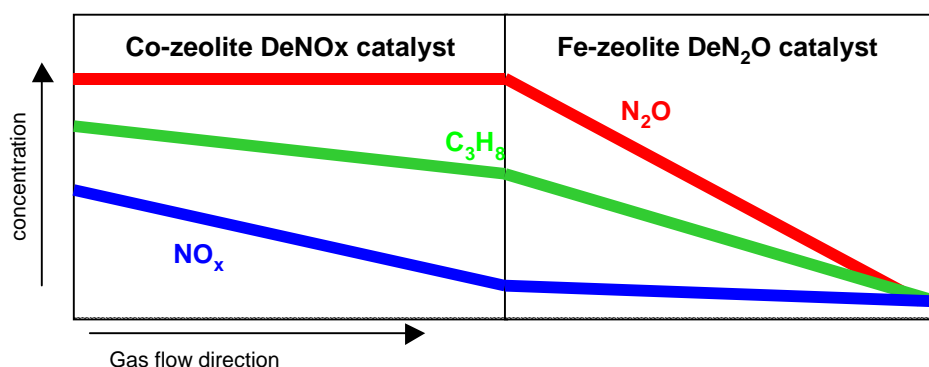


Figure 3.2 Concept of the two-catalyst system

On the first catalyst, Co-zeolite, NO_x reacts with propane. The input of propane is higher than necessary for NO_x reduction, so part of the propane reaches the second catalyst. On this Fe-zeolite catalyst the remaining propane reacts with N_2O .

On the first catalyst the following two (schematically represented) reactions take place:

- $\text{NO}_x + \text{C}_3\text{H}_8 \rightarrow \text{CO}_2 + \text{N}_2 + \text{H}_2\text{O}$
- $\text{C}_3\text{H}_8 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

The second reaction is undesired, because it leads to a lower availability of propane for the reaction with N_2O on the second catalyst. So the DeNO_x catalyst should be very selective for the first reaction. Figure 3.3A shows that at atmospheric pressure propane and NO_x conversion remain relatively low below 400°C . At a pressure of 4 bar(a) however, both the conversion of NO_x and propane are much higher at low temperatures. Somewhat above 350°C propane conversion becomes 90%, which means (with an input of 1000 ppmv C_3H_8) only 100 ppmv of propane is available for N_2O reduction on the second catalyst. In other words, at elevated pressure and temperatures above 350°C both reactions 1 and 2 are catalysed by Co-zeolite.

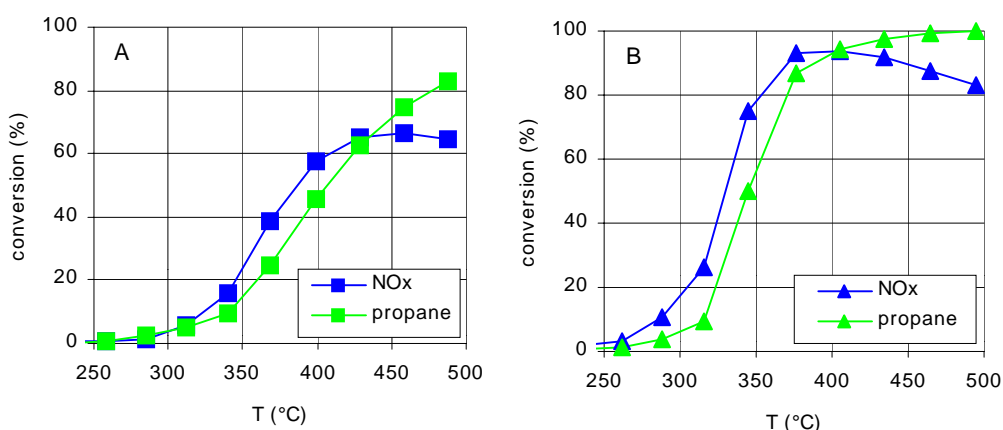


Figure 3.3 NO_x and propane conversion vs. catalyst inlet temperature on the Co-zeolite catalyst. Pressure is (A) 1 bar(a) and (B) 4 bar(a). Conditions, $S.V. = 120,000 \text{ h}^{-1}$, 1500 ppmv N_2O , 500 ppmv NO , 2.5 vol.% O_2 , 0.5 vol.% H_2O , 1000 ppmv C_3H_8 , balance N_2 .

On the second catalyst, the promoted Fe-ZSM-5 DeN₂O catalyst, the following reactions take place:

- $\text{N}_2\text{O} + \text{C}_3\text{H}_8 \rightarrow \text{CO}_2 + \text{N}_2 + \text{H}_2\text{O}$
- $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2$
- $\text{NO}_x + \text{C}_3\text{H}_8 \rightarrow \text{CO}_2 + \text{N}_2 + \text{H}_2\text{O}$
- $\text{C}_3\text{H}_8 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

Propane features in three reactions, which are all in competition with each other. Reaction (5) takes place at relatively low temperature, but at higher temperature reaction (3) takes over. This N₂O SCR reaction is in competition with propane combustion (6). At still higher temperatures propane reacts primarily with oxygen and N₂O is converted by direct decomposition (reaction 4). Pressure has a positive effect on all reactions.

In the reaction equations above, CO₂ is given as the final product. In many cases CO is also produced. The emission of carbon monoxide is unwanted and is removed by the addition of a very small amount of Pd to the second catalyst. Above 300°C the emission of CO is near zero.

3.3 Atmospheric pressure case

Different configurations of the two catalysts were tested [6] and one was selected as the most optimal at atmospheric pressure. The space velocity through the first (DeNO_x) catalyst bed is 30,000 h⁻¹. This is a compromise between a NO_x conversion that is as high as possible and a propane conversion that is as low as possible. The space velocity through the second (DeN₂O) catalyst is 20,000 h⁻¹.

Earlier studies [3,4] have shown that the amount of propane is the most important factor determining the cost effectiveness of the technique. Figure 3.4A shows the N₂O conversion for different amounts of propane. A decrease in the N₂O conversion curve between 350 and 400°C becomes apparent when the propane input is lower. This is caused by the fact that too little propane reaches the second catalyst.

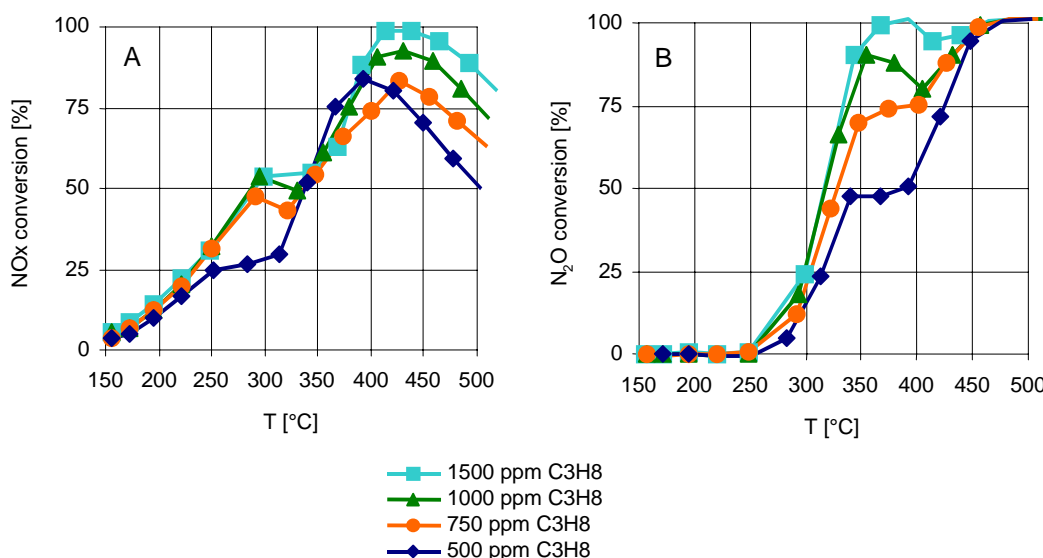


Figure 3.4 NO_x conversion (A) and N₂O conversion (B) at atmospheric pressure vs. reactor inlet temperature. Conditions: S.V. = 30,000 h⁻¹ (DeNO_x) and 20,000 h⁻¹ (DeN₂O), p = 1 bar(a), 1500 ppmv N₂O, 500 ppmv NO, 2.5% O₂, 0.5% H₂O

NO_x conversion (Figure 3.4B) is highest at around 400°C for all concentrations of propane. The maximum reduction level reached depends on the propane concentration. With 1500 ppmv of propane, the maximum NO_x conversion is almost 100%. When 500 ppmv NO_x is used, the maximum NO_x conversion is about 80%.

The cost efficiency is calculated by dividing the total annual costs by the amount of NO_x and N₂O (or CO₂ equivalents) removed. In other words, high reduction efficiency improves cost efficiency. From earlier experience we know that costs are for an important part determined by the amount of added propane. For the technical and economic evaluation 1000 ppmv propane was selected, which is expected to be the best compromise between low propane input and high NO_x and N₂O destruction efficiency. A high NO_x removal efficiency (>90%) is also necessary to meet future regulations.

3.4 High-pressure case

In the basis of design of this project (see section 5.2), the pressure in front of the expander is 10 bar(a). Our test equipment has been limited (until recently) to a pressure of 4 bar(a). Most experiments described below have been carried out at 4 bar(a). This implies that extrapolation of the results from 4 to 10 bar(a) is necessary. In the course of this project our set-up has been converted to allow experiments at 10 bar(a). The results are presented in this paragraph.

In Section 3.2 is described that the NO_x and propane conversion is strongly increased at higher pressures. This has as a consequence that the amount of propane available for the DeN₂O catalyst becomes critical. The resulting N₂O conversion curve is shown in Figure 3.5.

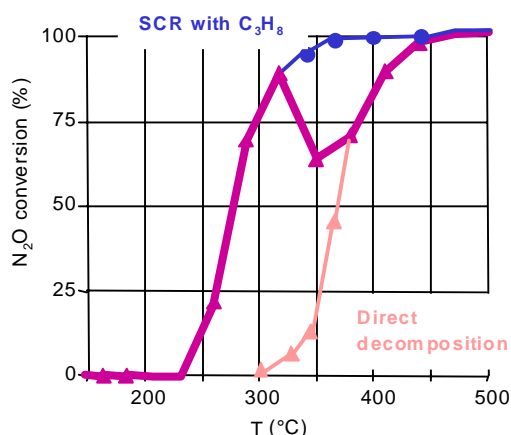


Figure 3.5 N₂O conversion at 4 bar(a) vs. reactor inlet temperature. Conditions: S.V. = 30,000 h⁻¹ (DeNO_x) and 20,000 h⁻¹ (DeN₂O), p = 1 bar(a), 1500 ppmv N₂O, 500 ppmv NO, 1500 ppmv C₃H₈, 2.5% O₂, 0.5% H₂O

At low temperatures enough propane exits the DeNO_x catalyst to make the reaction of propane with N₂O on the second catalyst possible. The catalyst follows the blue line, which represents the case when enough propane is present to carry out SCR of N₂O. Above 350°C all propane is consumed on the first catalyst, so N₂O is converted on the second catalyst by direct decomposition and follows the pink line in Figure 3.5.

A simple solution to this problem would be to increase propane input, but this will strongly increase the costs. So it must be accepted that, with most propane reacting on the first catalyst, only a small amount of propane reaches the DeN₂O catalyst. So direct decomposition will be the main reaction by which N₂O is removed.

The volume of the second catalyst is increased to increase the contact time of the N_2O molecules with the catalyst for direct decomposition. A scheme of the configuration for the high-pressure option is given in Figure 3.6.

For the direct decomposition to run at a sufficiently high rate, the temperature of the inlet of the second catalyst must be close to $400^\circ C$ [4]. The reaction of propane causes a temperature rise of the gas of about $33^\circ C$ per 500 ppmv of reacted propane. The amount of added propane should be high enough to preheat the gases to the required temperature.

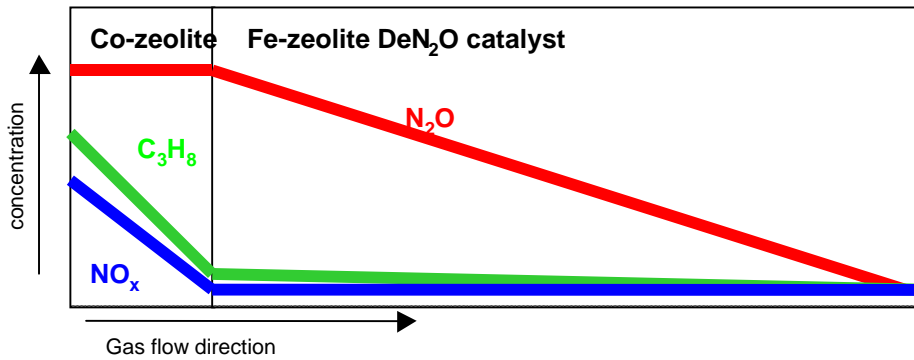


Figure 3.6 Concept of the two-catalyst system for the high-pressure case

The chosen configuration uses a space velocity of $120,000\text{ h}^{-1}$ through the $DeNO_x$ catalyst and $10,000\text{ h}^{-1}$ through the DeN_2O catalyst. Figure 3.7 shows that at least 1000 ppmv of propane is necessary to achieve more than 80% conversion of both N_2O and NO_x . In this experiment the pressure was 4 bar(a). Because the pressure plays such an important role the results at 4 bar(a) could not be used for extrapolation to 10 bar(a) as such. A kinetic model was designed to extrapolate the results on a more scientific basis (see Chapter 4).

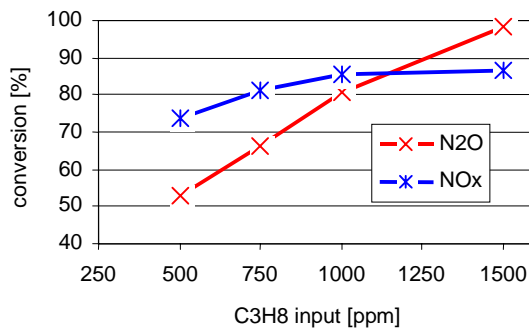


Figure 3.7 N_2O and NO_x conversion at 4 bar(a) vs. propane input concentration. Conditions: $S.V. = 120,000\text{ h}^{-1} + 10,000\text{ h}^{-1}$, 1500 ppmv N_2O , 500 ppmv NO , 2.5% O_2 , 0.5% H_2O

Simultaneously, the set-up was converted to make experiments at 10 bar(a) possible. Figure 3.8 shows the influence of pressure from atmospheric to 10 bar(a). Figure 3.8A shows that N_2O conversion at $350^\circ C$ is lower at higher pressures. This is caused by the increased consumption of the hydrocarbon on the $DeNO_x$ catalyst at high pressures.

The conversion of 1000 ppmv of propane on the first catalyst causes a temperature rise of the off gas of $65^\circ C$. When the inlet temperature is $350^\circ C$ and the reactor is adiabatic, the gas has a temperature of $415^\circ C$ when it enters the DeN_2O catalyst. From prior experiments with the same space velocity (see ref. [4]), a N_2O conversion of about 90% is expected. In Figure 3.8A the N_2O conversion is only about 60% at a temperature of $350^\circ C$ at the inlet of the first reactor. This confirms that the test reactor is not completely adiabatic (see ref. [4]).

Figure 3.8B shows that the conversion of NO_x increases with pressure.

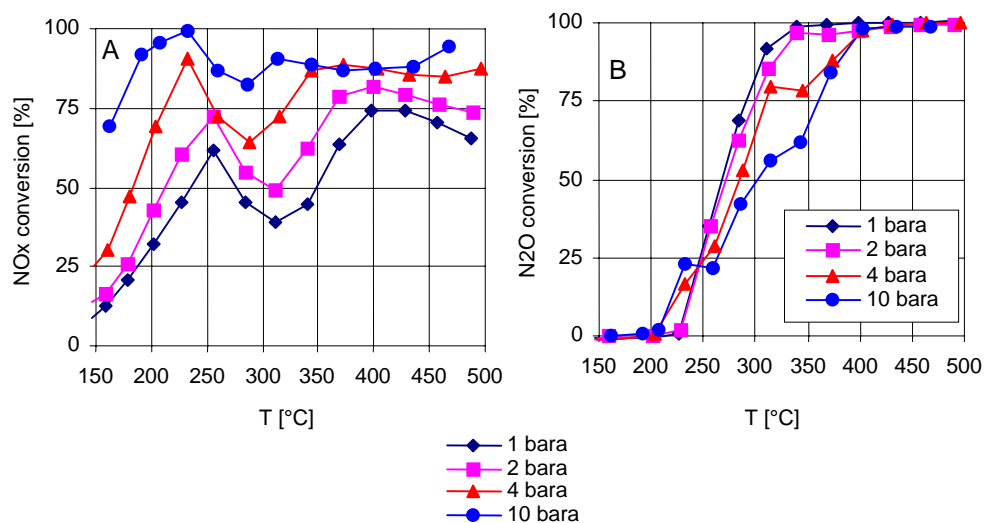


Figure 3.8 NO_x (A) and N_2O (B) conversion at var. pressures. Conditions: $S.V. = 120,000 \text{ h}^{-1} + 10,000 \text{ h}^{-1}$, 1500 ppmv N_2O , 500 ppmv NO , 1000 ppmv C_3H_8 , 2.5% O_2 , 0.5% H_2O

3.5 Methane as reducing agent

Previous research by ECN [4] has shown that methane (natural gas) is an interesting replacement for propane from an economic point of view. However, methane is much more difficult to activate than propane, with lower N_2O conversions and slip of methane as a consequence. Furthermore, the NO_x conversion was zero on the ECN Fe-zeolite catalyst when methane was used as a reducing agent.

In the literature catalysts are described that can reduce NO_x with methane, but the necessary temperatures are high ($>450^\circ\text{C}$) and conversions are relatively low. In the current project research was aimed at finding a catalyst that is able to activate methane at 350°C . In cooperation with another ECN project ($\text{CH}_4\text{-DeNO}_x$ for small scale energy generation devices) many different catalysts were synthesised and tested on the ECN micro-flow catalyst test rig. Relatively high NO_x conversions were reached with zeolite-based catalyst. Unfortunately, the stability of many of these samples proved to be a problem: conversion decreased rapidly with time on stream.

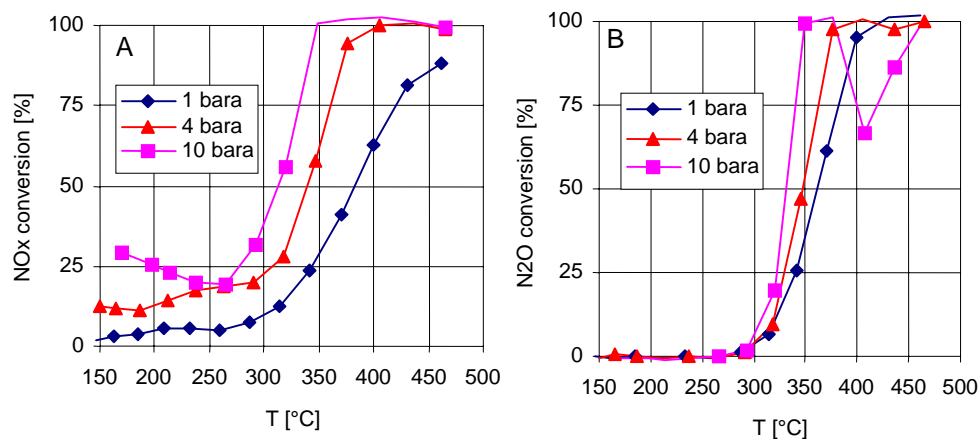


Figure 3.9 NO_x (A) and N_2O (B) conversion at var. pressures. Conditions: $S.V. = 20,000 \text{ h}^{-1}$ ($\text{CH}_4\text{-DeNO}_x$ catalyst) + $20,000 \text{ h}^{-1}$ (DeN_2O catalyst), 1500 ppmv N_2O , 500 ppmv NO , 2500 ppmv C_3H_8 , 2.5% O_2 , 0.5% H_2O

A catalyst was found with a sufficiently high activity at 350°C. The stability of the system was tested at 350°C and after an initial small decrease, the conversions were stable for 100 h. This catalyst was combined with the standard Pd-Fe-ZSM-5 DeN₂O catalyst. The space velocity through each catalyst was 20,000 h⁻¹ and methane input was 2500 ppmv.

Figure 3.9 shows the conversions of NO_x and N₂O at different pressures. Conversion of both N₂O and NO_x increase with higher pressure. At 10 bar(a) the destruction efficiency of NO_x and N₂O is close to 100% at 350°C. At higher temperatures N₂O conversion decreases to 66% at 410°C, which is caused by the methane being consumed on the first catalyst (the same effect as described in the preceding section for propane).

At 10 bar(a), the conversion of methane at 350°C is 75%, which means that about 600 ppmv methane leaves the catalyst bed unreacted. When 1500 ppmv of methane was used (instead of 2500 ppmv), conversions of NO_x and N₂O at 350°C are practically the same, and methane slip is reduced to approximately 400 ppmv. We expect that changing the relative amounts of catalyst can further reduce methane slip.

It must be noted that the CH₄-DeNO_x catalyst is still under development and especially its long-term stability has to be confirmed as yet.

4. KINETIC MODEL OF THE DENO_x/DEN₂O SYSTEM

A kinetic model was composed based on simplified kinetics of the SCR-HC reduction reactions of NO_x and N₂O. The motivation for the development of the model was the fact that only a limited number of tests at 10 bara could be performed in ECN's mini-flow reactor. It was necessary to carefully plan these tests. The model was a tool to predict the behaviour of a reactor system and therefore to determine which test conditions should be used in order to yield the maximum information from the (limited number of) tests.

The overall objective was to determine the most useful conditions for tests at 10 bara. Technical objective was to have an accurate description of the dual-bed system. Guidelines for the development of the model were:

- The predictions of the model must be accurate within the experimental domain that is used, with small extrapolations.
- The predictive value for variations in pressure is most important. It must enable extrapolation from tests at 1–5 bara (experimental domain) to 10 bara.
- Kinetics do not necessarily have to be comprehensive or realistic. Any set of kinetic expressions is acceptable as long as the model predicts results correctly.

The model employs the following reactions. In the segments of the reactor, the reactions are applied in three phases:

1. Free sites (*) on the surface react with nitrous oxide from the gas phase generating inactive O-* sites:
$$* + \text{N}_2\text{O} = \text{N}_2 + \text{O-*} \text{ (surface oxidation)} \quad (\text{R1.1})$$
2. Removal of inactive sites to active, free sites by means of three reactions.
$$\text{O-*} = * + \frac{1}{2} \text{O}_2 \text{ (oxygen desorption)} \quad (\text{R2.1})$$
$$\text{C}_3\text{H}_8 + \text{O-*} = \text{CO}_2 + \text{H}_2\text{O} + * \quad (\text{R2.2})$$
$$\text{NO} + \text{O-*} = \text{NO}_2 \quad (\text{R2.3})$$
3. Reaction on free sites:
$$\text{N}_2\text{O} + * = \text{N}_2 + * \text{ (N}_2\text{O reduction)} \quad (\text{R3.1})$$
$$\text{C}_3\text{H}_8 + \text{NO} + * = \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O} \text{ (SCR of NO}_x\text{)} \quad (\text{R3.2})$$
$$\text{NO}_2 = \text{NO} + \text{O-*} \quad (\text{R3.3})$$

In the first phase, the reaction is presumed to be complete and at the end of the phase 1, the catalyst surface is completely covered with inactive sites (O-*). The reactions in the other two phases are kinetically controlled using Arrhenius type expressions. The stoichiometry of reaction R2.2 and reaction R3.2 can be varied and adjusted as fitting parameters.

The reactor system is composed of two catalyst beds in series with the following assumptions:

- the reactors are adiabatic,
- pressure is constant,
- each catalyst bed is separated into a series of 250–1000 segments,
- each segment has constant conditions, following the perfectly stirred tank reactor model,
- in each segment, using inlet conditions, first reaction rates are calculated, then concentration changes, then heat production, then the temperature change,
- the changed concentrations and temperature are the outlet conditions,
- the inlet conditions of the reactor are the inlet conditions of the first segment,
- the outlet conditions of a segment are the inlet conditions of the next segment,
- the outlet conditions of the last segment are the outlet conditions of the catalyst bed,
- the outlet conditions of the first catalyst bed are the inlet conditions of the second catalyst bed.

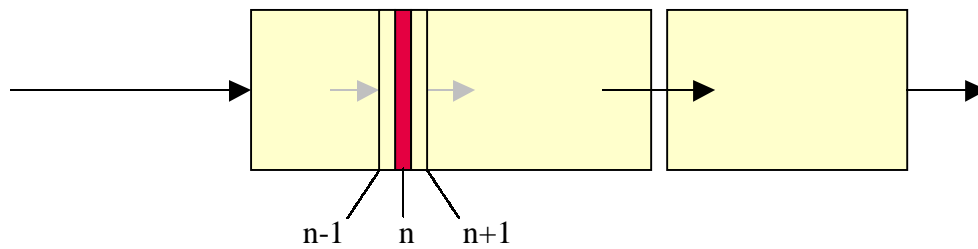


Figure 4.1 Diagram of the two serial catalyst bed and the segments into which they are divided

The model is programmed as a set of Excel worksheets, where input parameters can be entered in certain cells. The input parameters are classified in:

1. known constants, e.g., heat capacities, reaction enthalpies,
2. unknown constants, e.g., pre-exponential rate constants, activation energies,
3. reaction parameters, e.g., catalyst mass, inlet concentrations, inlet temperature, pressure.

The reaction parameters are variable for each experiment. The known and unknown constants apply to all experiments, but the latter are fitted using the experimental data. The fitting has been done using visual inspection and comparison with the experimental data.

Figure 4.2 is an example where the model predicts N_2O conversion at different pressures the combine $DeNO_x/DeN_2O$ system. For comparison, experimental data are added.

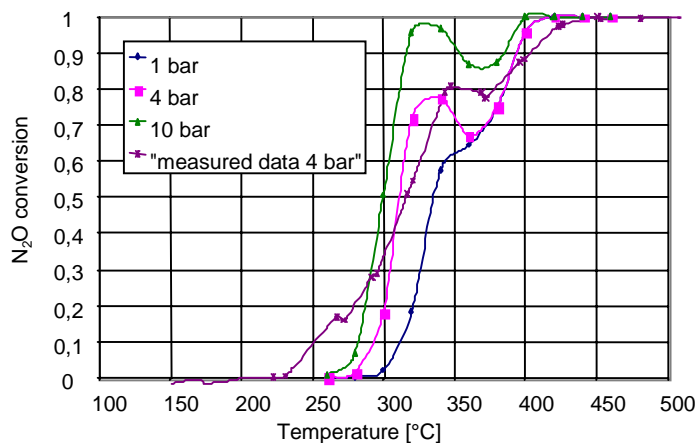


Figure 4.2 Activation plots generated by the model, compared to experimental data; 500 ppm NO, 1500 ppm N_2O , 1000 ppm C_3H_8 , space velocities $120,000 h^{-1}$ ($DeNO_x$ catalyst) and $10,000 h^{-1}$ (DeN_2O catalyst)

The model predicts the form of the N_2O conversion curve, including the decrease in conversion between 350 and 400°C, rather accurately. The congruency with measured data at 4 bar(a) is acceptable. The model produces steeper curves because it presumes complete adiabatic conditions while the experiments are done in a reactor with a substantial heat loss.

With respect to pressure dependency, the model predicts an enhanced conversion more or less proportional with increasing pressure. Figure 3.8 shows measured data under the same conditions, and an opposite trend is observed. The reasons for this poor are as yet unknown. They may be found in the deviation of our experimental set-up from the ideal conditions assumed in the model.

5. TECHNICAL AND ECONOMIC EVALUATION

5.1 Introduction

Studies into the potential of the ECN DeN₂O technology in the market of N₂O reduction in nitric acid production plants showed that the direct decomposition technology is promising for high pressure (10 bar(a)) and high temperature (over 400°C) applications, with cost efficiencies in the range of €0.3 - 1.0 per ton CO₂ equivalents reduced. For existing production plants at moderate temperature levels (lower than 400°C) or if the available space for retrofit is limited, hydrocarbon assisted SCR could be attractive with cost efficiencies in the range of €1.4 - 2.5 per ton CO₂. Yearly costs for SCR are mostly determined by the costs of the consumed reducing agent (LPG or natural gas).

As not all nitric acid production plants are already equipped with conventional DeNO_x systems, a hydrocarbon assisted combined SCR DeNO_x and DeN₂O system could be more attractive (cost effective) than separate DeNO_x and DeN₂O systems. Therefore, ECN explored the DeNO_x potential of the catalyst and commissioned Emission Care to execute a technical and economic feasibility study for a hydrocarbon assisted combined DeNO_x and DeN₂O system.

5.2 Basis of Design technical and economic assessment

The technical and economic assessment is based on an average tail gas flow and composition of Dutch nitric acid plants:

Tail gas flow	: 200,000 Nm ³ /hour
N ₂ O concentration	: 1500 ppmv
NO _x concentration	: 500 ppmv (as NO)

For application upstream an existing expander (high pressure case), a pressure of 10 bar(a) and a temperature of 350°C is available. For application downstream an existing expander (atmospheric pressure case), a pressure of 1 bar(a) and temperature of 100°C is available.

Investment costs incorporate engineering, procurement and installation of equipment and catalyst at site (assuming a clear construction area is available) and 1 year of construction interest. Unforeseen items are incorporated using a contingency factor of 15%. For the high pressure case, retrofit costs are estimated using a retrofit factor of 1½. This figure was derived of VROM figures for retrofitting DeNO_x systems in the Dutch chemical industry.

Exploitation costs have been calculated according to the VROM method, using the Capital Recovery Factor method for assessment of the capital costs at an interest rate of 7%. A depreciation period of 10 years is used for both electro-mechanical equipment and civil works. For the ECN catalyst, a depreciation period of 5 years is used. Exploitation costs include recovery losses due to decreased expander performance.

The cost efficiencies are attributed to CO₂ equivalents according to the TEWI-guidelines. All costs are either contributed to N₂O or NO_x reduction only. The other reduced component is then considered as a positive side-effect.

5.3 Atmospheric Pressure Case

The atmospheric pressure system is operated at an inlet temperature of 395°C, using a combined reactor system (lateral flow catalytic reactor) with an overall space velocity of 12,000 h⁻¹ and dosing of 1000 ppmv LPG. Using this configuration, 90% NO_x reduction and 90% N₂O reduction can be achieved.

The system incorporates a heat recuperator to preheat the tail gas to the required inlet temperature with tail gas leaving the combined reactor system, LPG storage and dosing and a start-up burner. In case of an emergency shut-down, a bypass system is available. The conceptual process set-up is displayed in Figure 5.1.

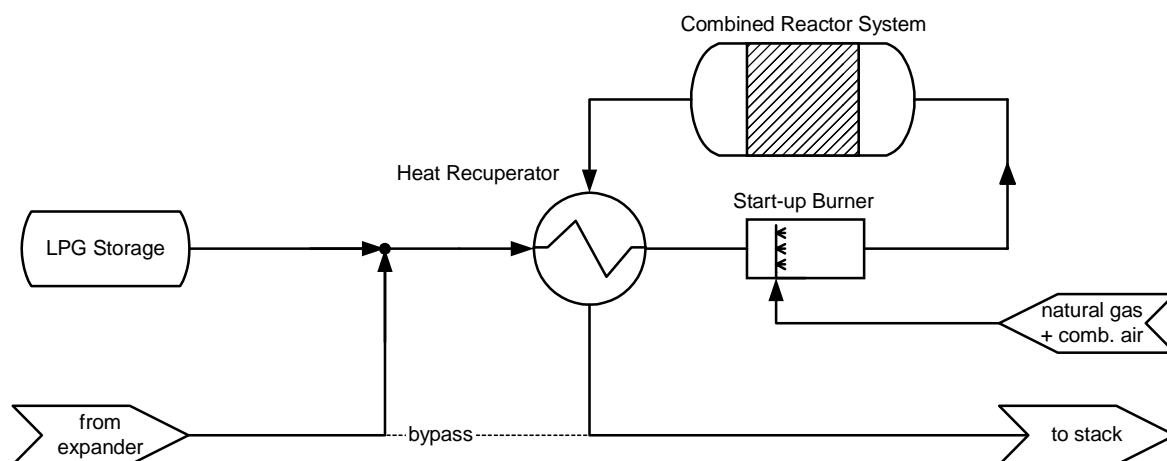


Figure 5.1 Conceptual process set-up atmospheric combined DeNO_x and DeN₂O system

The atmospheric combined DeNO_x and DeN₂O system is characterised by:

- an annual reduction of 1.5 kton NO_x and 4.2 kton N₂O, equivalent with a reduction of 1,280 kton CO₂ equivalents,
- a pressure drop of approximately 120 mbar, leading to a production loss equivalent with €300,000 per year,
- consumption of 3,100 ton LPG per year, equivalent with €1.2 M per year,
- investment costs of €5.6 M,
- a cost efficiency of either €1.8 per kg NO_x or €0.6 per kg N₂O, equivalent to €2.1 per ton CO₂ equivalents.

Due to fluctuations in the LPG price, the cost efficiency for N₂O reduction might vary between €1.9 and 2.3 per ton CO₂ equivalents.

5.4 High Pressure Case

The high pressure system is operated at a pressure of 10 bar(a) and an inlet temperature of 350°C, using a combined reactor system (lateral flow catalytic reactor) with an overall space velocity of ± 10,000 h⁻¹ and dosing of 1000 ppmv LPG. At this configuration, 90% NO_x reduction and 90% N₂O reduction is achieved.

The system incorporates LPG storage and dosing, an inline mixer to ensure an even distribution of LPG and a cooler to remove the excess heat generated in the combined reactor system. In case of an emergency shut-down, a bypass system is available. The conceptual process set-up is displayed in Figure 5.2.

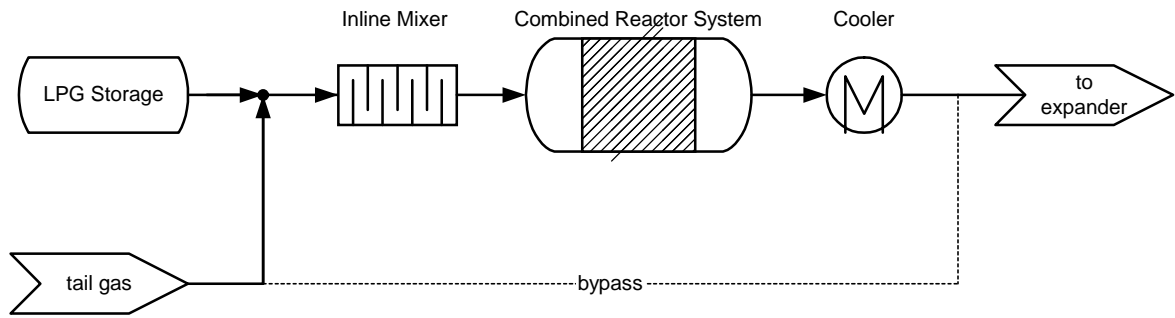


Figure 5.2 Conceptual process set-up high pressure combined $DeNO_x$ and DeN_2O system

The high pressure combined $DeNO_x$ and DeN_2O system is characterised by:

- an annual reduction of 1.5 kton NO_x and 4.2 kton N_2O , equivalent with a reduction of 1,280 kton CO_2 equivalents,
- a pressure drop of approximately 160 mbar, leading to a production loss equivalent with €400,000 per year,
- consumption of 3,100 ton LPG per year, equivalent with €1,2 M per year;
- investment costs of €6.2 M,
- a cost efficiency of either €1.7 per kg NO_x or €0.6 per kg N_2O , equivalent to €2.0 per ton CO_2 equivalents.

Due to fluctuations in the LPG price, the cost efficiency for N_2O reduction might vary between €1.8 and 2.2 per ton CO_2 equivalents.

5.5 Reference Case

The combined $DeNO_x$ and DeN_2O system has to compete with a combination of a conventional ammonia assisted $DeNO_x$ system and a separate DeN_2O system. For the given basis of design, the most cost effective combination is an ammonia assisted $DeNO_x$ system upstream the expander and a LPG assisted DeN_2O system downstream the expander, using 500 ppmv LPG.

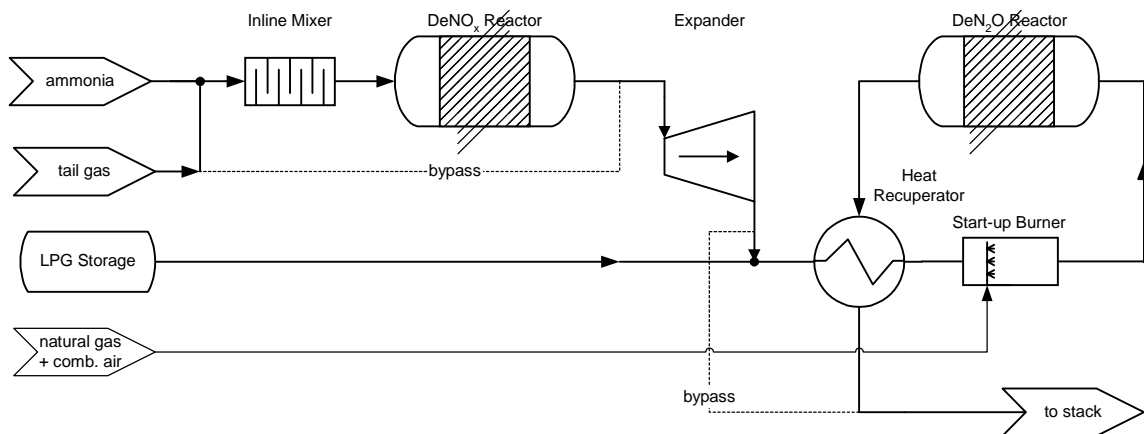


Figure 5.3 Conventional ammonia assisted $DeNO_x$ system combined with LPG assisted DeN_2O system

The conventional ammonia assisted DeNO_x and hydrocarbon assisted DeN₂O system is characterised by:

- an annual reduction of 1.5 kton NO_x and 4.2 kton N₂O, equivalent with a reduction of 1,280 kton CO₂ equivalents,
- a pressure drop of approximately 200-210 mbar, leading to a production loss equivalent with €520,000 per year,
- consumption of 640 ton ammonia and 1,550 ton LPG per year, equivalent with €0.7 M per year,
- investment costs of €6.9 M,
- a cost efficiency of either €1.8 per kg NO_x or €0.6 per kg N₂O, equivalent to €2.1 per ton CO₂ equivalents.

5.6 Evaluation of the combined DeNO_x and DeN₂O system

In the table presented below, the obtained results for both conventional and combined DeNO_x and DeN₂O abatement systems are summarised.

Table 5.1 *Results for conventional and combined DeNO_x and DeN₂O systems, based on 90% reduction of 500 ppmv NO_x and 90% reduction of 1500 ppmv N₂O*

Post	Unit	Reference System	Hydrocarbon assisted	
			atm. pres.	high pres.
Investment Cost	10 ⁶ €	6.9	5.6	6.2
Annual Cost	10 ⁶ €/yr	2.7	2.7	2.6
Yearly Reduction	kton NO _x /year	1.5	1.5	1.5
	kton N ₂ O/year	4.2	4.2	4.2
Cost efficiency	kton CO ₂ eq./year	1.280	1.280	1.280
	- NO _x	€/kg	1.8	1.7
- N ₂ O	€/kg	0.6	0.6	0.6
- CO ₂ eq.	€/ton	2.1	2.1	2.0

By combining two separate systems into one combined DeNO_x and DeN₂O system, the total investment costs can be reduced up to 1.3 M €. The effect of depreciation on the yearly costs is however moderate.

As the minimum dosing of LPG is limited by the wanted NO_x conversion and the required operating temperature, the combined DeNO_x and DeN₂O system consumes more LPG than the reference system. Therefore, the annual cost for consumption of reducing agent are higher.

The total annual costs of atmospheric and high pressure combined DeNO_x and DeN₂O systems are of the same order of magnitude as the total annual cost for the reference system, and therefore the cost efficiencies are comparable. The cost efficiency for CO₂ reduction of the combined DeNO_x and DeN₂O system is slightly above the cost efficiency of separate hydrocarbon assisted DeN₂O systems (€1.4 - 2.5/ton CO₂), but has an extra side effect of reducing 1.5 kton NO_x per year.

As the reference system consists of two separate systems, each system can be operated independently without influencing each other. An ammonia assisted DeNO_x system is also a proven technology. Therefore, if the combined DeNO_x and DeN₂O systems has no significant financial benefits, for this basis of design case two separate systems will be preferred.

For specific plants however, the combined DeNO_x and DeN₂O system could be preferred above the reference system:

- At temperature levels upstream the expander of 250°C or less, ammonia assisted DeNO_x costs are increased.
- At temperature levels upstream the expander of 400°C or higher, high pressure ammonia assisted DeNO_x is not feasible, where an atmospheric or high pressure combined system still can be applied.
- If high pressure retrofit is not possible due to physical limitations, in most cases downstream applications still can be applied.
- Low NO_x concentrations allows reduction of the amount of reducing agent required. The impact on costs of LPG consumption can be quite considerable. However, high NO_x concentrations require high LPG dosing, thus favouring the application of ammonia assisted DeNO_x systems.
- The combined system could also be implemented in applications outside the nitric acid industry where NO_x and N₂O reduction is desired, ammonia is not available or allowed, and the presence of the hydrocarbon reducing agent is affirmed.

Therefore, possible cases for combined DeNO_x and DeN₂O system application seem available, and can be influenced by a.o. local legislation, flexible instruments etc.

5.7 Impression hydrocarbon assisted DeNO_x system

The costs for hydrocarbon assisted DeNO_x systems have been derived assuming a system is installed, prepared for combined NO_x and N₂O abatement, but without the N₂O catalyst modules. Those costs have been compared with costs for ammonia assisted DeNO_x systems, solely installed for NO_x abatement.

The annual costs of hydrocarbon assisted DeNO_x systems are a factor 2-3 higher than the annual costs for ammonia assisted DeNO_x systems in nitric acid plants: 2-2.5 M €/year instead of 0.8 M €/year. Therefore, the cost efficiency for hydrocarbon assisted DeNO_x is the same order of magnitude less: €1.4-1.7 per kg NO_x instead of €0.5 per kg NO_x.

The difference in annual costs is mainly due to increased investment costs and consumption of reducing agent. To compete with the ammonia assisted DeNO_x systems, consumption of reducing agent should be lowered significantly.

Nevertheless, the cost efficiency of hydrocarbon assisted DeNO_x systems is well below the maximum level which is found reasonable in the Netherlands, €4.5 per kg NO_x reduced. The hydrocarbon assisted DeNO_x technology might be of importance in situations where the application of ammonia assisted DeNO_x systems is less economic attractive or wanted, e.g. in case of atmospheric end-of-pipe applications, limitations to the storage of ammonia, relative high tail gas temperatures etc.

6. CONCLUSIONS

The goal of the project was to develop and test a system on laboratory scale for N₂O and NO_x removal in a single reactor. The results described in this report show that this goal has been achieved. A cobalt-containing zeolite DeNO_x catalyst and the ECN iron-containing zeolite catalyst are placed in series and both at atmospheric and high pressure high NO_x and N₂O conversions are achieved.

- *Atmospheric pressure case:* The most optimal configuration is a space velocity of 30,000 h⁻¹ through the DeNO_x catalyst and 20,000 h⁻¹ through the DeN₂O catalyst. The lowest possible input of the reducing agent propane is 1000 ppmv. Conversions of N₂O (original concentration 1500 ppmv) and NO_x (original concentration is 500 ppmv) are around 90%.
- *High-pressure case:* At high pressure the NO_x and propane conversion on the DeNO_x catalyst, which is first in line, is strongly increased. The downside of this effect is that the amount of propane that reaches the second catalyst for reaction with N₂O is very low. So direct decomposition is the main reaction taking place on the DeN₂O catalyst, instead of SCR. The chosen configuration is a space velocity of 120,000 h⁻¹ through the DeNO_x catalyst and 10,000 h⁻¹ through the DeN₂O catalyst. Like in the atmospheric pressure case 1000 ppmv of propane is necessary.

The two cases described above were used in the technical and economic evaluation. A conceptual process flow scheme has been designed and the investment and annual costs were calculated. The total annual costs have been divided by the total amount of NO_x reduced or the total amount of N₂O reduced. Furthermore, the cost efficiencies are attributed to CO₂ equivalents according to the TEWI-guidelines. All costs are either contributed to N₂O or NO_x reduction only. The other reduced component is then considered as a positive side-effect.

The costs are compared to a reference case, consisting of a conventional NH₃-DeNO_x installation in front of the expander and a propane-DeN₂O installation downstream the expander. The cost efficiencies (around 2 € per ton CO₂ equivalents or 1.8 € per kg NO_x) are equal for the high-pressure case, the atmospheric pressure case and the reference case.

The industry is expected to have a preference for the reference case, because of the higher flexibility of a two-reactor system and the fact that NH₃-DeNO_x is a proven technology. However, for specific plants (e.g. with a very low tail gas temperature or with limit space for retrofit) propane-based DeNO_x and DeN₂O in a single reactor may be an attractive option. The main reason for the single reactor not being more cost effective than the reference case is the rather high input and costs of propane as compared to ammonia.

Methane has also been studied as a more cost-efficient alternative for propane. A catalyst developed by ECN has been shown to give high NO_x conversions at 350°C and at 4 bar(a) using methane as a reducing agent. Combination of this catalyst with the ECN DeN₂O catalyst may give a system that removes NO_x and N₂O at considerably lower costs. Methane (in the form of natural gas) is widely available and less expensive than propane.

The project generated valuable knowledge on the reactions taking place on both the DeNO_x and DeN₂O catalysts. This information has been used to design a kinetic model of the two-catalyst system. The model is used to assist in the extrapolation of the results at 4 bar(a) to 10 bar(a). The model gives a good description of the trends taking place. However, comparison to tests at 10 bar(a) show that the model has a too optimistic prediction of the positive effect of pressure on N₂O and NO_x conversion.

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