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Catalytic removal of NO_x from total energy installation flue-gases for carbon dioxide fertilization in greenhouses

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Abstract

A catalytic process, based on urea as a reactant to remove NO_x from the exhaust gases of total energy installations driven by gas engines has been developed. A prototype has been successfully tested using a commercial gas engine.

Keywords: NO_x removal

1. Introduction

In Dutch greenhouses a large and growing amount of energy is used. In the eighties there was a yearly consumption of about 2.5 billion m^3 natural gas and about 400 billion kWh electrical power respectively. In the early nineties this has risen to ca. 4 billion m^3 and ca. 800 billion kWh [1]. Both the government and the horticulture branch are looking for ways to decrease the energy costs. By using total energy (TE) installations both these costs and pollution can be reduced significantly. This is illustrated by the increasing amount of TE installations in Dutch greenhouses. In 1990 there was about 200 MW_e installed. This figure has increased to 700 MW_e in 1994 and is expected to further increase up to 1500 MW_e by the year 2000 [2].

Crop growth can be stimulated by efficiently controlling the growth factors light, heat and CO_2. Research has shown that increasing the CO_2 concentration can stimulate the crop growth [3,4]. Fig. 1 shows that an extra growth of up to ca. 30% can be obtained. At the moment, heat and CO_2 is mainly supplied by a central heating boiler fired by natural gas. Electricity, for artificial lighting, is obtained from the public grid. By using gas fired TE installations 55% of the total energy is converted into heat and 35% into electricity. Hence, these installations can be used for both heating the greenhouses and supplying power for artificial lighting. If not necessary in the greenhouse the electricity can also be fed back to the public grid. The efficiency can even be further increased by using the CO_2 from their flue gases. However, these gases contain too much NO_x and ethylene to be led into the greenhouse untreated. Consequently, the exhaust gases from the (now smaller) central heating boiler are still used for this purpose, even when there is no heat demand!

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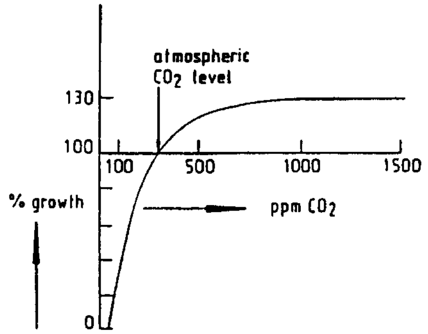

Fig. 1. Crop growth as a function of the CO_2 concentration ([3]).

At the moment almost all TE installations are of the lean-burn type. Engines of this type use more air than is necessary for complete combustion, resulting in a significantly reduced NO_x emission. An important parameter in this respect is the so called 'air factor' λ, the molar air to fuel ratio. A factor $\lambda = 1$ denotes stoichiometric combustion whereas $\lambda > 1.2$ denotes operation under lean-burn conditions. To illustrate this: the NO_x concentrations may vary from 200 ($\lambda = 1.4$) up to 6000 ppm ($\lambda = 1$).

Even lean-burn engines produce too much NO_x to be used for CO_2 fertilization. Table 1 shows the emission guidelines for the various components, present in these gases. These values pertain to a desired CO_2 level in the greenhouse of 800 ppm.

To further clean the flue-gases several options are available. De Noord [6] summarises 28 different processes. Only 11 are suitable for practical application [7]. These can be divided into 3 categories. (i) Catalytic reduction. Here, NO_x is converted into N_2 and H_2O. This is realized by selective, ammonia or urea based catalytic reduction (SCR) or non-selective catalytic reduction (NSCR); in the latter case a three-way catalyst in combination with flue gas recirculation is used [8]. (ii) Oxidation, where NO is oxidized to NO_2 followed by a water wash to nitric acid. (iii) CO_2 decomposition, where the flue gases are washed with potassium carbonate followed by recovery from bicarbonate.

Table 1
Maximum concentrations of some toxic chemicals in flue gases [2,5]

Component	Standards		
	$\lambda = 1$ (ppm)	$\lambda = 1.55$ (ppm)	g/GJ
NO	45.6	28.5	15.0
NO_2	24.5	15.3	12.2
C_2H_4	1.16	0.73	0.35
NH_3	39.6	24.7	7.2

2. Selective catalytic reduction

In the Delft NO_x/Urea Process SCR is applied with urea as the reductant. In the industrial process ammonia is usually used for this purpose. However, for safety reasons pure ammonia cannot be applied in greenhouses due to the (chemically) unexperienced personnel. Urea, however, is widely available and is easy to handle and store. In the past urea *prills* were applied [9]. A drawback of using these prills was accumulation of solid urea-polymerisation by-products. By a direct injection of a urea/water solution in the flue gases this can be avoided. Moreover, a significant reduction of the investment costs can be obtained.

Fig. 2 shows the basic configuration of the Delft NO_x/urea process. For optimal operation the temperature of the flue gases must be between ca. 300 and 400°C. In the present study 325°C was chosen. The gas enters the reactor in the atomizer chamber. The aqueous urea solu-

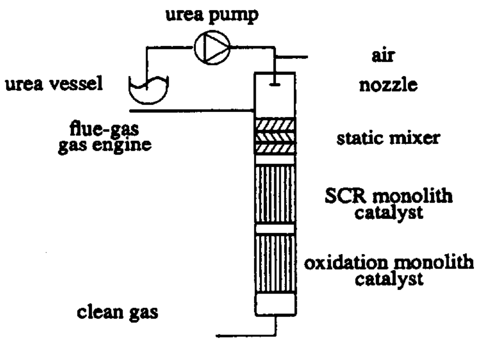

Fig. 2. The Delft NO_x/Urea Process.

tion is pumped to the top of the reactor where it is atomized using compressed air and an air-blast-nozzle. The urea then decomposes into ammonia-like products which are well mixed with the flue gases by static mixers. The reaction with NO_x occurs in a (Degussa DN32) monolith reactor. The catalytically active material is $V_2O_5/TiO_2/W_2O_3$. In a second monolithic reactor (Hereaus D30), carbon monoxide and unburned hydrocarbons are converted to CO_2. This is very important with respect to the removal of ethylene which is very toxic for the crop. Also a possible ammonia excess is oxidized depending on the catalyst either to N_2 or NO. Obviously, the first reaction is preferred, although in the latter case (as with the Hereaus D30 monolith) the amounts of NO produced are far below the level required.

3. Results

To test the urea process, a 4 cylinder 1.6 l gas engine was used (FORD 2274E). This engine drives a generator which delivers a continuous maximum power of 29 kW at 3000 rpm. The engine produces a maximum flow of 60 m^3 (NTP)/h from which a sidestream of 4.4 m^3 (NTP)/h is led through the reactor resulting in a GHSV = 5100 h^{-1}.

First the performance of the system was tested under stationary conditions. The air factor λ was varied from rich to lean-burn conditions where for each λ the urea dosing rate has been kept constant and was calculated after measuring the NO_x concentration in the engine exhaust. Here, a urea:NO ratio of 1:2 was used.

The composition of the gases was measured on various places in the set-up. A flow of about 8 l^3 (NTP)/min was led through a heated tube to the analysis instruments. About 1 l (NTP)/min was directly fed to the NH_3 analyser (infrared analyser equipped with a heated optical cell for continuous measurement). The rest of the gas was dried with a Peltier cooling element and fed to the various other analysing instruments, i.e., a chemiluminescence analyser for continuous measurement of NO and NO_2, a paramagnetic continuous O_2 analyser, a combined CO and CO_2 continuous analyser and a gaschromatograph analyser with flame ionisation-detector (FID) for discontinuous measuring of unburned hydrocarbons.

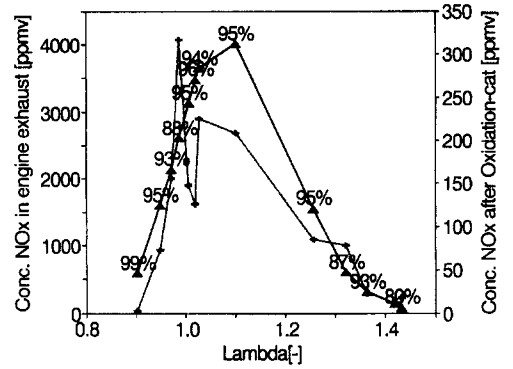

Fig. 3. NO_x concentration before and after the $deNO_x$ catalyst. The numbers in the graph denote the conversions.

For each set point, there was no detectable ammonia slip. Fig. 3 shows that very high conversions (over 90%) can be achieved with this system. However, since the guidelines are not determined by conversion but by absolute concentrations (ca. 50 ppm, see Table 1) there may still be some problems for non-lean-burn engines. For lean-burn engines a conversion of ca. 85% may be high enough whereas for a NO_x output of 1000 ppm a conversion of 95% should be achieved.

Another problem arises from the transient NO_x concentration in the flue gases which may be caused by control algorithms in the motor-management system of the engine such as a λ-control device. For lean-burn engines this spread in concentration is not a problem. This is illustrated in Fig. 4 where the inlet concentration showed a spread of ca. 100 ppm which was eliminated completely. For application on non-lean-burn engines a simple PID controller using an (expensive) NO_x analyzer was applied successfully as can be seen in Fig. 5. Fig. 6 shows that the flue gases from the gas engine contain too much ethylene. However, the oxidation cata-

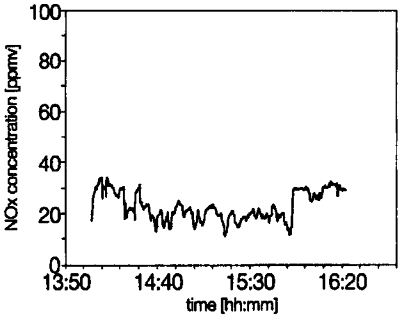

Fig. 4. NO_x concentration at a constant urea dosing rate. The inlet concentration is ca. 400 ppm NO_x.

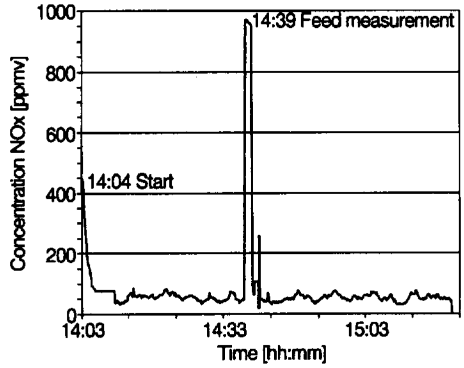

Fig. 5. NO_x concentration using a process control algorithm. The NO_x concentration at the inlet is 1000 ppm.

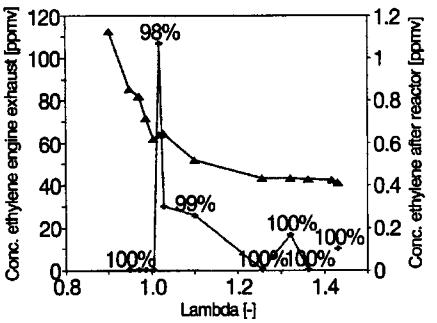

Fig. 6. C_2H_4 before and after the catalysts. The numbers in the graph denote the conversions.

lyst is able to remove this almost completely (conversion > 98%; 0.2–1 ppm, left). Also, the carbon monoxide concentration is too high. A characteristic value is ca. 350 ppm. The oxidation catalyst provides an almost complete reduction (> 99%).

4. Scale-up

After ca. 50 operating hours the atomizer was inspected and was found to be still in good condition. Atomizing at a larger scale is possible without any doubt. The monolith reactor was still very clean. There was no blockage by ash particles. Moreover, the pressure drop was very low (lower than 4 mbar using two 1 l monoliths with a diameter of 92.5 mm and 400 cells per square inch). By choosing a monolith reactor the scale-up is very simple: the monolith dimensions should be chosen such that the residence time is maintained.

A full scale installation was designed and an economical evaluation was carried out for a 9 hectare greenhouse and an engine exhaust flow of 5285 (n)m^3/h. The system is operated for 4900 h/year. The costs appeared to be surprisingly low. The return on investment and the pay out time are estimated to be 700% and 0.5 year, respectively. Hence, the system is beneficial both from an economical and an environmental point of view.

5. Conclusions

The Delft NO_x/Urea Process was tested at GASTEC and can be applied for cleaning flue gases of gas engines from TE installations for CO_2 fertilization purposes in greenhouses. The urea atomization option is robust. All toxic components are sufficiently removed and the system has a low pressure drop. Moreover, the system is very cheap. Recently, a full scale installation has been designed, built by the Dutch company 'Inodes' and successfully put into operation.

This pertains to the lean-burn engines, applied in the Dutch greenhouses. For application to so called $\lambda = 1$ engines, the NO_x conversion must be extremely high and in order to avoid ammonia slip a process control system must be implemented.

Acknowledgements

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