

Catalytic removal of NO_x from total energy installation flue-gases: process design and development

R.G.H. Smeets^{*}, H.P. Calis, P.M. Lugt, C.M. van den Bleek

Faculty of Chemical Technology and Materials Science, Delft University of Technology, Julianalaan 136, 2628 BL Delft, Netherlands

Abstract

The flue-gases from total energy installations can be used for CO₂ fertilization in greenhouses. However, the gases contain too much toxic chemicals to be led into the greenhouses untreated. At Delft University of Technology a process has been developed for the removal of these toxins. This so called 'Delft NO_x/urea process' has been tested successfully downstream of a natural gas fired engine. Our group has described that the process could be well used for so called lean-burn engines. However, for non-lean-burn engines, which have a very high NO_x output (1500 ppm), the required NO_x conversion was not reached. Which was caused by high NO_x concentration. Hence, the process should be optimized further for this purpose. Especially, the decomposition of urea should be given more attention. This paper focuses on this aspect. The decomposition has been investigated both theoretically and experimentally.

Keywords: NO_x removal

1. Introduction

In the Dutch greenhouses gas fired total energy (TE) installations are used for heating and lighting. It would be attractive to use the CO₂ content of the flue-gases for crop fertilization. Van Berkel [1] has shown that an extra growth of ca. 30% can be obtained. However, the flue-gases contain too much NO_x and ethylene which are toxic for plants ([2]).

At Delft University of Technology a catalytic aftertreatment process, based on selective catalytic reduction (SCR), has been developed for the removal of these toxic compounds ([2,3]). This so called 'Delft NO_x/urea process' has been tested successfully. At the moment, a de-

sign is made for full-scale implementation downstream of a TE installation.

2. Process design and development

In the Delft NO_x/urea process SCR is applied with urea as the reactant to remove NO_x. Urea is, unlike the widely used ammonia, easy to handle and store. This makes urea very suitable for unexperienced greenhouse personnel. Fig. 1 shows a schematic representation of the Delft NO_x/urea process. An aqueous urea solution is directly injected in a reactor where at a high temperature ($T = 400^{\circ}\text{C}$) urea decomposes into ammonia-like products ([2]). After mixing with the flue-gases over a set of static mixers, the stream enters a monolith (V₂O₅-TiO₂-W₂O₃ reactor. Here, NO_x is converted into harmless

^{*} Corresponding author.

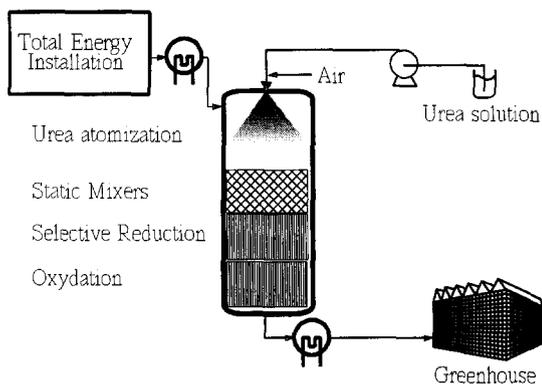


Fig. 1. The Delft NO_x/urea process.

nitrogen and water. The SCR monolith is followed by a second monolith where traces of CO, methane and ethylene are converted into CO₂. Moreover, a possible ammonia slip is oxidized here into NO_x. Finally, the flue-gases are cooled and led to the greenhouse where the CO₂ is used for crop growth stimulation.

Lugt et al. [3] described that the process could well be used for so called lean-burn engines. For implementation after a non-lean-burn engine the required low NO_x concentration at the outlet side of the reactor could not be obtained, because the NO_x conversion, under the same conditions, should be significantly higher in that case. The NO_x concentrations in the flue-gases of the engines were ca. 500 and 1200 ppm, respectively. To satisfy the emission guidelines, the NO_x concentration at the reactor outlet should be ca. 50 ppm [3]. Hence, the required conversions should be 90% and 96%,

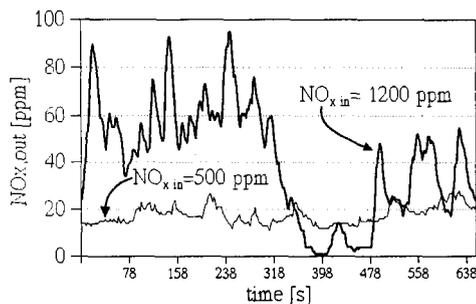


Fig. 2. NO_x reduction with an urea-solution (stoichiometric conditions).

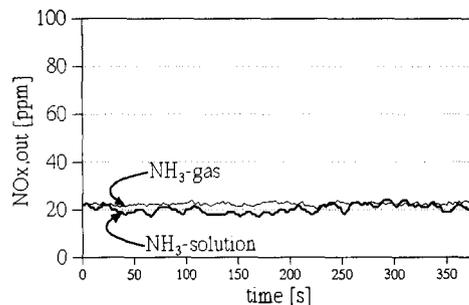


Fig. 3. NO_x reduction with ammonia gas and an ammonia solution (NO_x_{in} = 1200 ppm, and stoichiometric conditions).

respectively. It will be clear that the latter can not be obtained easily.

Fig. 2 shows lab-scale experiments (GHSV = 5000 h⁻¹, T = 400°C) where both lean- and non-lean-burn engines are simulated, using a model gas (NO in air). It appears that for a lean-burn engine the emission guidelines can be satisfied. However, the figure also shows that for the non-lean-burn situation the desired conversion is not achieved. This could probably be ascribed to incomplete decomposition of urea.

To investigate this assumption, instead of the urea solution an aqueous ammonia solution and ammonia gas were injected. Fig. 3 shows the results of the non-lean-burn engine simulation experiment. The figure shows that the desired NO_x conversion is now easily achieved. Consequently, the urea decomposition, in the prior experiment, was indeed not complete.

Hence, in order to implement the process downstream of a non-lean-burn engine, the urea atomization and decomposition should be given more attention.

3. Atomization of the urea solution

According to Wypkema [2], urea decomposes instantly when a temperature of approximately 300°C is reached. If the water is not fully evaporated when the gas enters the SCR monolith, part of the urea stays at the wet bulb temperature, which is of course far below 300°C. It will be clear that the water evaporation is the

limiting step in this process, since heating up the water vapour to 300°C will be very fast. Therefore, it is essential to know the minimal length to be created inside the reactor for a complete evaporation of the water whereafter full decomposition of urea can take place almost instantly. The determination of this length can be performed both experimentally and theoretically and will be described in the next sections.

3.1. Experimental determination of the urea decomposition rate

The urea decomposition rate can be determined by measuring the ammonia concentration inside the reactor as a function of place.

For this purpose, the free space between static mixers and monolith was enlarged and the reactor was equipped with two ammonia sample points, as shown in Fig. 4.

Fig. 5 shows the results of experiments simulating TE installations of the lean-burn and non-lean-burn type. The NO_x-concentrations at the entrance of the reactor are approximately 500 and 1000 ppm, respectively. By spraying a stoichiometric amount of urea into the reactor (1 mol of urea reacts with 2 mol of NO), it appears that directly downstream of the static mixers the ammonia concentration is low and consequently the urea decomposition is also very low before

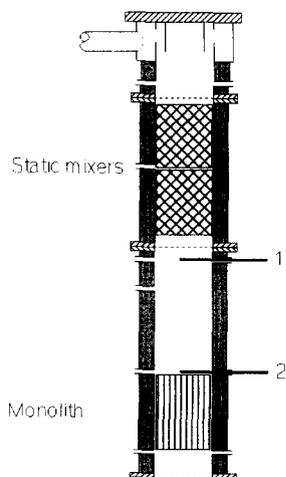


Fig. 4. Experimental setup.

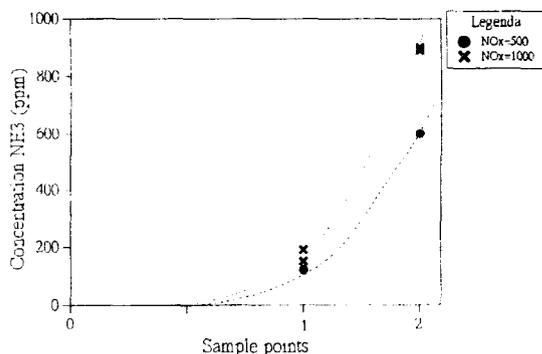


Fig. 5. Urea decomposition experiments.

this point. Whereas the ammonia concentration at the second sample point equals almost the theoretically highest achievable NH₃-concentration. Hence, complete decomposition has taken place between the two sample points. In Fig. 5, the ammonia concentration profiles have been estimated at two points only, assuming the process to be linear. Two points are not enough to give an optimisation. So, in the future more measurements will be done.

3.2. Theoretical determination of the urea decomposition rate

For the theoretical determination of the urea decomposition rate, it is assumed that the length necessary for water evaporation is the limiting step. To calculate this length a model is used as proposed by Crowe [4].

When the droplets encounter the gas stream after injection, transfer takes place by three mechanisms: mass, momentum and energy transfer. Consider the droplet shown in Fig. 6,

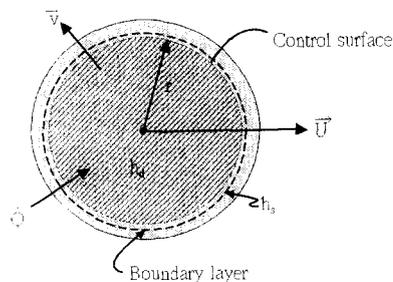


Fig. 6. An evaporating droplet.

whose centre of mass is moving with a velocity U . A mass with a velocity v and an amount of heat Q is transferred through the control surface around the droplet.

The mass transfer of an evaporating droplet is described by Fick's law of diffusion, in which the mass flux is proportional to the concentration gradient.

$$\frac{dm}{dt} = Sh \pi \rho D_v d (C_\infty - C_s) \quad (1)$$

The influence on droplet mass transfer by the presence of neighbouring droplets is in general translated into a reduction of the Sherwood number. However, this is difficult to incorporate in a model and will not be taken into account here.

The droplet momentum transfer can easily be written by Newton's second law,

$$F = m \frac{dU}{dt} \quad (2)$$

The most significant aerodynamic force acting on the droplet is the drag force caused by the relative velocity between particle and gas. At Reynolds numbers less than unity, Stokes' law is applicable; that is,

$$F = 3\pi\mu d(V - U) \quad (3)$$

The droplet heat transfer is a function of the droplet's change of internal energy i_d and the change of enthalpy due to evaporation,

$$\frac{dQ}{dt} = m - \frac{di_d}{dt} - (\bar{h}_s - h_d) \frac{dm}{dt} \quad (4)$$

Analogous to mass transfer, the driving mechanism for heat transfer is the temperature difference between the droplet surface and the drying medium (the flue-gases). According to Fourier's law, the rate of heat transfer is proportional to the temperature gradient, so

$$\frac{dQ}{dt} = Nuk\pi d(T_\infty - T_s) \quad (5)$$

These equations have been implemented in a numerical solver and were used for determining the necessary length of evaporation and thus

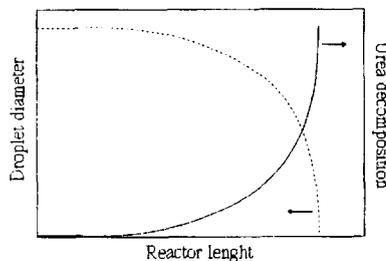


Fig. 7. Relation between reactor length and droplet size reduction and urea decomposition.

urea decomposition. Fig. 7 shows the relation between droplet diameter and reactor length.

The shape of the calculated curve and the measured curves in Fig. 5 seem to correspond. Furthermore, the figure shows that the decomposition rate is increasing fast in the reactor. This is most significant with respect to designing the process. The figure learns that the major decomposition occurs at a relatively small part of the reactor at the outlet side. Consequently, reducing the length may lead to a drastic reduction of the conversion.

4. Conclusions

The Delft NO_x /urea process can well be used for cleaning flue-gases of lean-burn engines. However, for non-lean-burn engines the necessary NO_x conversion should be higher. Therefore, it is essential to create enough length in the reactor for urea decomposition. This reactor length is determined both experimentally and theoretically on the basis of some preliminary experiments. More experiments will be done to check these conclusions. Finally, the calculations learn that the reactor length is very critical. A small reduction of this length can lead to a drastic reduction of the conversion.

5. Symbols

c	concentration
d	droplet diameter
D_v	Diffusion coefficient

F	force
h	enthalpy
i	internal energy
k	thermal conductivity
m	droplet mass
Nu	Nusselt number
Q	heat
Sh	Sherwood number
t	time
T	temperature
U	droplet velocity
v	gas velocity
ρ	density
μ	viscosity
Subscripts	
d	droplet
s	droplet surface
∞	in the gas

Acknowledgements

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