

# NO<sub>x</sub> from combustion

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## Formation and Suppression by means of Recycling Burners

Nitrogen oxides and SO<sub>2</sub> are the primarily harmful emissions from firing and combustion processes. A reduction of these wastes is among those tasks of environmental protection with top priority. Where as the formation of SO<sub>2</sub> as a combustion product of the fuel sulphur is unavoidable and has to be eliminated from the flue gas, our knowledge of the formation of nitrogen oxides enables us to avoid such a formation or to reduce it substantially. This paper discusses the reduction of NO<sub>x</sub> in recycling burners and offers proof of it. A sketch about the forming mechanism of nitrogen oxides is given at first for a better understanding.

NO<sub>x</sub> from combustion form almost exclusively as NO. It changes to NO<sub>2</sub> at temperatures below 620°C and sufficient residence time with oxygen from its surroundings and becomes visible as brownish-red plume at concentrations of above 550 ppm. Because of its diverse forming mechanisms we distinguish between thermal NO from the nitrogen of the combustion air and chemical NO from the fixed nitrogen in the fuel.

### Thermal NO<sub>x</sub>

Thermal NO is formed by O<sub>2</sub> and N<sub>2</sub> at high temperature and sufficient residence time. This formation of thermal NO is called Zeldovic mechanism after its discoverer and behaves according to the equation given in fig. 1.  
(Culmination of the NO formation is reached at approximately 2000° C and decreases drastically with increasing temperatures.)

The time necessary to form NO is taken to be infinite and thus not considered. In reality, NO is formed between 0 and 5 seconds almost proportional to the time of reaction. If the time of reaction = 0, then NO = 0.

It is possible to predict the quantity of thermal NO<sub>x</sub> assuming ideal conditions (adiabatic combustion). However, this is not possible for real combustion systems with different disruptions and thus no quantitative prognosis can be made. On the other hand, it is possible to predict tendencies which have a positive or

negative effect on the formation of NO, i.e. in what respect

- increasing concentration of N<sub>2</sub> respectively O<sub>2</sub>
  - increasing residence time
  - increasing temperature
- favor the formation of NO. This means that the formation of thermal NO during combustion can be reduced by the following measures:
- reducing the excess air
  - reducing the residence time
  - reducing the combustion temperature.

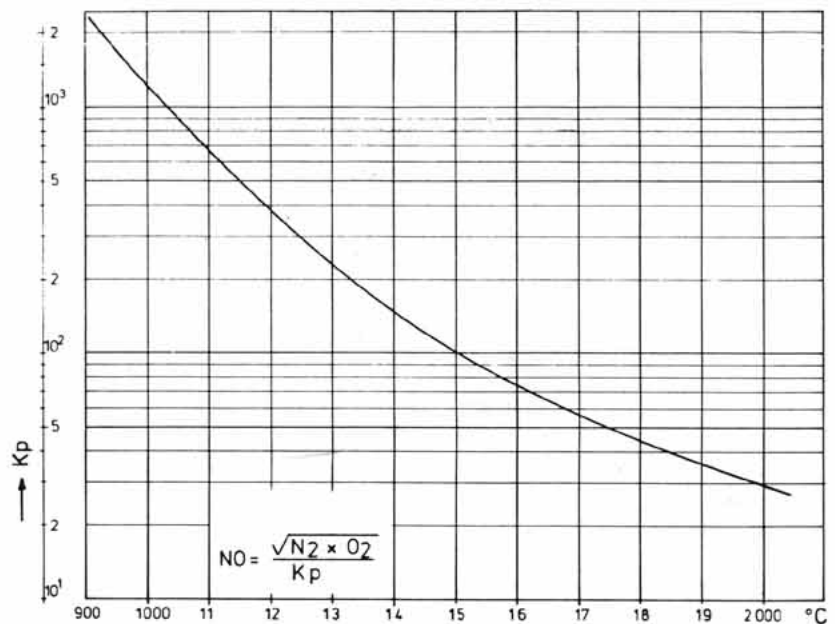


Fig. 1: Formation of NO at infinite reaction time depending on temperature and partial pressure of N<sub>2</sub> and O<sub>2</sub>

### Chemical NO<sub>x</sub>

Chemical NO<sub>x</sub> is formed through the reaction of fixed nitrogen in the fuel and oxygen from the combustion air. At a level of 0,2 percentage by weight of nitrogen in the fuel the amount of chemical NO<sub>x</sub> accounts for about half of the entire NO<sub>x</sub> in the flue gas. Hence, chemical NO<sub>x</sub> is no less significant than thermal NO<sub>x</sub>. The formation mechanism for chemical NO is far more complex than for thermal NO. For this reason, its intermediate reactions under participation of fuel radicals are not yet fully understood. As a consequence, fig. 2 shows only those main reactions of the pathway of fuel nitrogen necessary for better understanding.

### Functioning of recycling burners

In the recycling burner described in the following (fig. 3 and 5) the injector effect of the combustion air intake of the burner causes hot flue gases from the combustion chamber to flow back through the recirculation duct into the adjoining mixing tube. The fuel is injected into the hot flue gases and is thus predigested before it comes into contact with the combustion air. Under the influence of the recycled flue gases the fuel is at first thermally upgraded and broken down into smaller molecules below that temperature which would allow its cracking. In this process, at first radicals and then aldehydes are formed. (fig. 4)

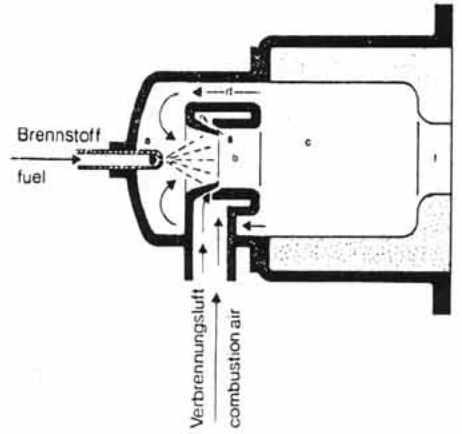


Fig. 3: Recycling burner with constricted combustion chamber outlet: a) air nozzles, b) mixing tube, c) combustion chamber, d) recirculation duct, e) fuel nozzle, f) burner outlet

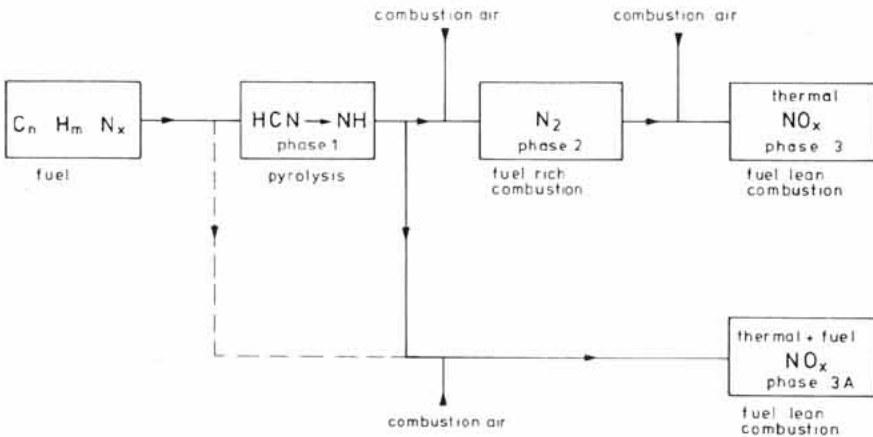


Fig. 2: Pathway of the fuel nitrogen during combustion.

A prerequisite for the transformation of fuel nitrogen into N<sub>2</sub> as shown in fig. 2 is a thermal and chemical upgrading of the fuel before and during phase I. Unevaporated fuel or soot would transfer fixed nitrogen into phase 3 and cause the formation of fuel NO<sub>x</sub>.

The formation mechanism of fuel NO<sub>x</sub> requires the following measures in order to avoid nitrogen oxides:

- a thermal and chemical upgrading of the fuel
- avoiding formation of solid carbon (soot)
- a 2-step combustion with deficiency of air in the first step.

### Effects on the formation of NO

Compared to conventional burners which mix fuel and air directly before the formation of the flame, the combustion process in recycling burners as described above reduces the formation of NO for the following reasons:

#### Thermal NO<sub>x</sub>

Even in a more or less complete combustion with excess of air, the primary combustion still takes place under fuel rich conditions. Thus the temperatures as well as the O<sub>2</sub> content are minimized in that phase of the combustion which is decisive for the formation of NO.

The O<sub>2</sub> partial pressure in the combustion is always below 21 % by vol, (by recycling flue gas in a ratio of 40 % of the combustion air O<sub>2</sub> = 15 % by vol). In an open combustion chamber (fig. 5) already partially cooled flue gas is recycled and thus leads to a reduction of the maximum combustion temperature.

The combustion process in recycling burners allows a high combustion chamber capacity equivalent to a short residence time.

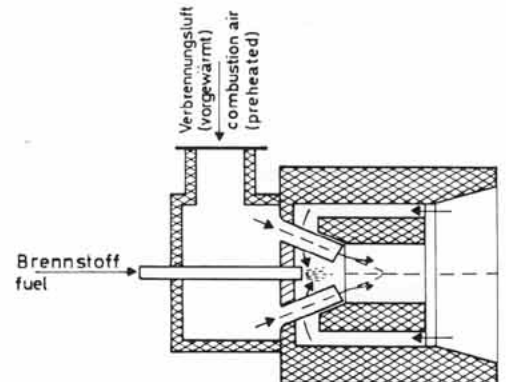


Fig. 5: Recycling burner with open combustion chamber

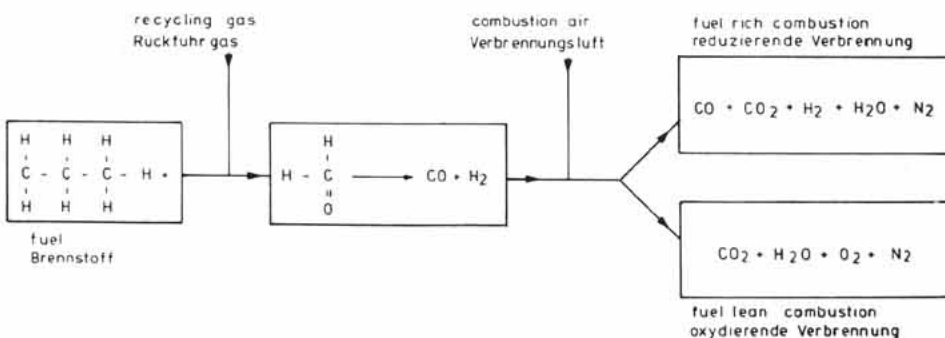


Fig. 4.: Scheme of aldehydic combustion.

### Chemical NO<sub>x</sub>

The fuel is chemically upgraded through the influence of hot recycling gas. Combustion occurs through the formation of radicals and aldehydes, avoiding the formation of carbon.

Since soot does not even form with strong air deficiency (fuel/air ratio 0.6 . . . 0.7) requirements for a 2-step combustion are fulfilled.

### Process firing

Wastes containing nitrogen, for example Amine, Pyridine etc. from chemical production cause a high content of (fuel) NO<sub>x</sub> in a 1-step combustion. Extensive combustion tests were made for design and optimization of a plant for the incineration of waste Monomethylamin (CH<sub>3</sub>NH<sub>2</sub>). The formation of fuel NO<sub>x</sub> can be substantially suppressed through a 2-step combustion whereas a 1-step combustion would in NO<sub>x</sub>-contents of up to 3000 ppm in the flue gas. (fig. 7 and 8)

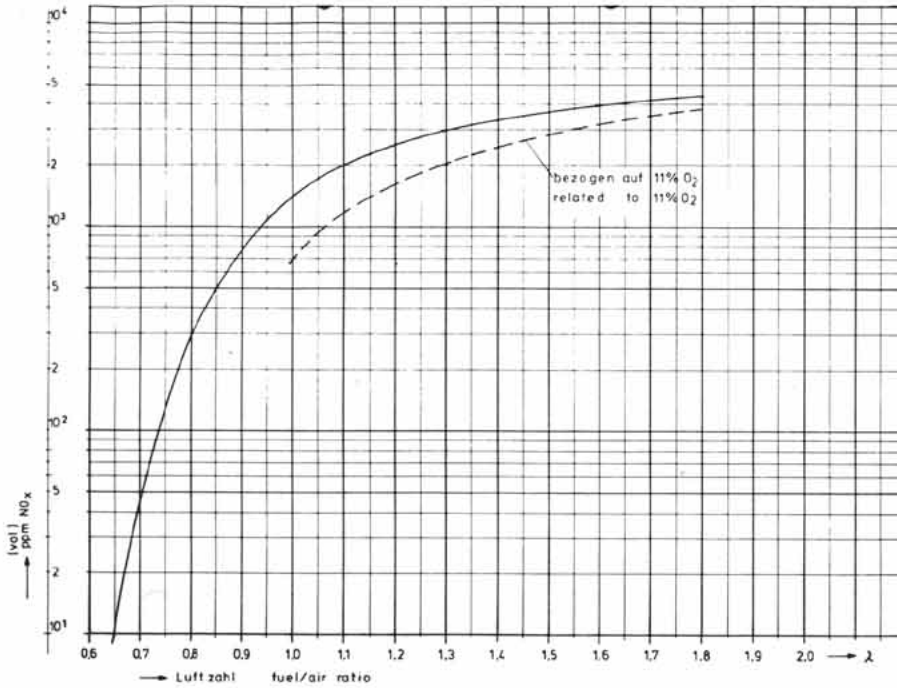


Fig. 7: Formation of NO<sub>x</sub> burning Monomethylamine (CH<sub>3</sub>NH<sub>2</sub>) in a recycling burner (as to fig. 4) depending on fuel/air ratio.

### Practical results

#### Boiler firing

At the university of Aachen, a small burner for conventional warm water boilers was developed (see fig. 3). The maximum NO<sub>x</sub> content emitted by this burner at a capacity of 0.65 gph fuel oil is 43 ppm. At the same capacity and method of operation, the average NO<sub>x</sub> values of nine investigated conventional burners with yellow luminous flame was nearly 2 times as high with a medium of 84 ppm.

In Japan research to improve recycling burners was government supported because of their favorable NO<sub>x</sub> emission. Because of the open combustion chamber and the thus resulting in recycling of already partly cooled flue gas, an NO<sub>x</sub> value of 40 ppm was obtained, amounting to only approximately 10 % of the NO<sub>x</sub> emission of conventional burners at a comparable duty.

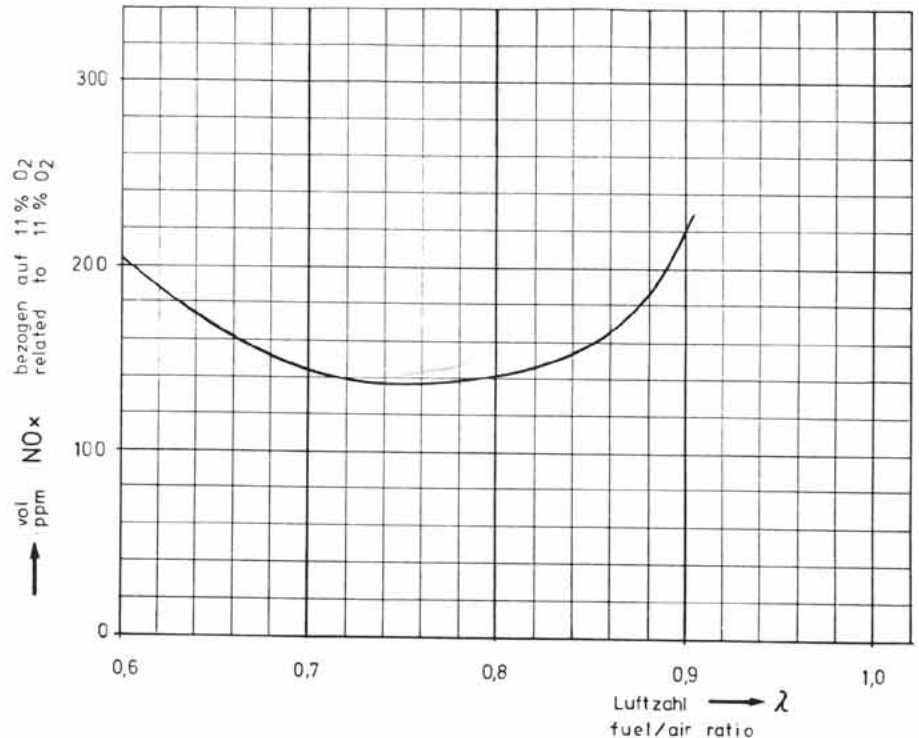


Fig. 8: Formation of NO<sub>x</sub> in the second step of combustion burning Monomethylamine (CH<sub>3</sub>NH<sub>2</sub>) related to fuel/air ratio in the first step of combustion. (fig. 7)

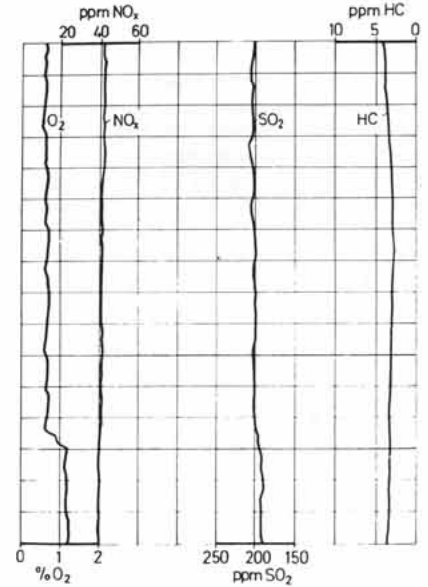


Fig. 6: Flue gas analysis of a recycling burner as to fig. 5 on a steam boiler burning heavy fuel oil (type A, Japanese standard).

## Conclusion

The addition of flue gas during combustion reduces the formation of  $\text{NO}_x$ . The recycling of substantially cooled-off flue gas and its addition to the combustion air mainly reduces the formation of thermal  $\text{NO}_x$  (at approx. 30 %) (9). By contrast, in the recycling burner described above, the formation of thermal  $\text{NO}_x$  as well as fuel  $\text{NO}_x$  is largely suppressed on account of the upgrading of the fuel with hot gases before a contact with the combustion air takes place.

## References

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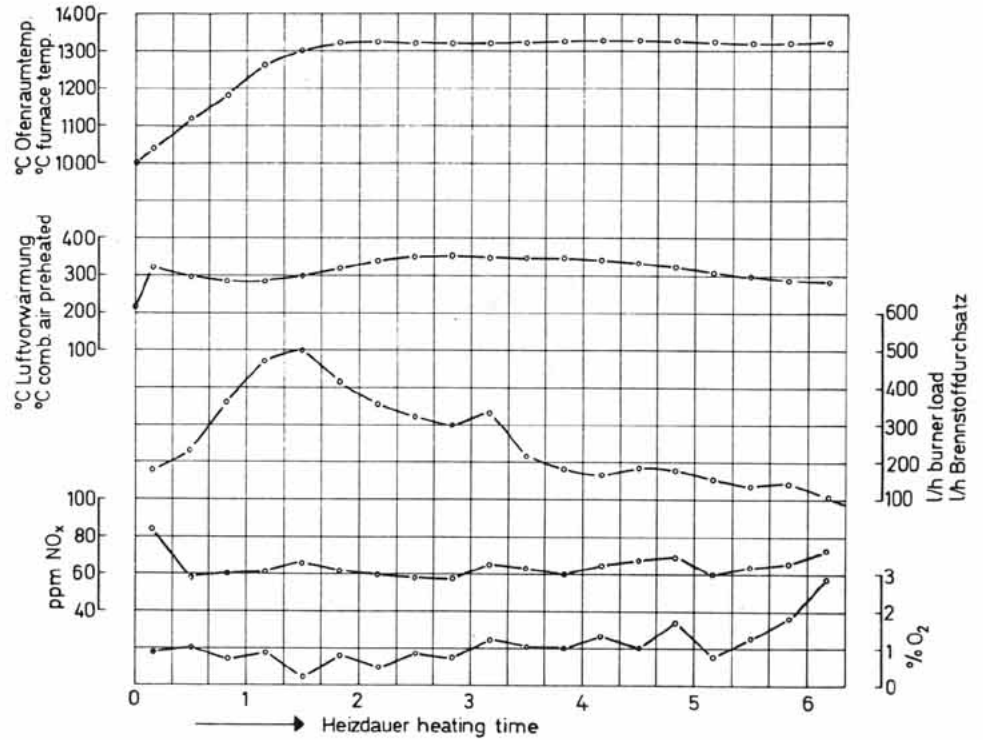


Fig. 9:  $\text{NO}_x$  formation of a recycling burner on a soaking furnace working with preheated combustion air an heavy fuel oil.