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ABSORPTIVE SEPARATION OF NO FROM DILUTE OFF-GAS

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ABSTRACT

With regard to its negligible absorption properties, the separation of nitrogen monoxide from dilute off-gas is limited to bench-scale experiments. Investigation has been centered on improving the rate of absorption by the use of complex-forming additives based on iron(II) compounds. Further efforts have been made to improve the separation efficiency by the use of reactive additives. Due to the low reactivity of nitrogen monoxide, these attempts did not succeed.

The oxidation of moderately concentrated off-gas with ozone and the absorption of the so-formed nitrogen dioxide have been reported. Technical as well as economical considerations do not permit the application of the process to the treatment of dilute off-gas.

The principle underlying this process led to the investigation of direct oxidation of the off-gas under electrical discharge followed by absorption with aqueous diamide solution. Temperature and moisture of the off-gas have been considered, in addition to various feed contents of nitrogen monoxide. The results of this investigation show that direct oxidation of nitrogen monoxide by corona discharge is possible. The rate of conversion increases with increasing gas velocity, accompanied by a decreasing specific energy consumption. Applied to tunnel off-gas purification, the direct oxidation route seems to offer promising technical boundaries as it is accompanied by efficient particle separation.

INTRODUCTION

The investigation of NO absorption has centered on improving the rate of absorption by the use of complex-forming additives based on Fe(II) [1,2,3]. Further efforts were made to improve the separation efficiency by the use of reactive additives [4]. Table 1 details the qualitative evaluation of additives that have been investigated. As shown by the results, the reduction of NO has been observed only when the system Fe(II)/SO_2 is applied. But several additives do react with NO_2 and preferably cause the formation of nitrogen.

Technical application of the absorptive removal of nitrogen monoxide from off-gas demands oxidation of the species within the separation process. The oxidation of moderately concentrated off-gas with ozone and the absorption of the so-formed nitrogen dioxide has been reported [5]. Technical as well as economical considerations do not recommend the application of this process to the treatment of dilute off-gas.

These boundaries led to the investigation of an oxidation process based on direct oxidation of the off-gas under electrical discharge followed by absorption with aqueous diamide. The objective of the program is the evaluation of the energy consumption of the oxidation process under different conditions (e.g., moisture content of the off-gas, feed content of nitrogen monoxide, electrical power generation and geometry of the ionizer).

FUNDAMENTALS OF ELECTRICAL GAS DISCHARGE

Gaseous discharge at ambient pressure can be observed between the corona starting voltage and the breakdown voltage. Peek derived an empirical equation for the calculation of the electrical field strength E_0 for gaseous discharge at ambient pressure when using plain wires [6]:

$$E_0 = 3 \cdot 10^6 \cdot \delta + 9 \cdot 10^4 \cdot \sqrt{\frac{\delta}{r_0}} \tag{1}$$

Where

E_0 = corona start potential [V/m]

δ = correction factor [-]

r_0 = radius of the discharge electrode [m]

The correction factor considers the pressure of operation and the temperature in relation to normal conditions:

$$\delta = \frac{p \cdot T_0}{p_0 \cdot T} \tag{2}$$

TABLE 1. REACTIVE ADDITIVES USED FOR NO_X ABSORPTION

Reactive Additive	*NO Absorption*	*NO_2 Absorption*	*NO_x Absorption*
Water	a	b	a
0.23 M Hydroquinone, acidified with 2 M H_2SO_4	a	c	a
0.5 M Oxalic acid	a	b	a
1 M Diamide	a	c	c
Cr(II)/Cr(III) system	a	b	b
Urea	a	b	a
Sulfanilic acid	a	b	b
0.25 M $NaSO_3$	a	b	b
Acidified FeSO4 + simultaneous SO2-absorption	b	b	b
0.04 M Morpholine	a	b	b

a : No absorption occurs with the reactive solvent.
b : $\leq 50\%$ of NO_x absorption occurs in an impinging system.
c : $> 50\%$ of NO_x absorption occurs in an impinging system.

Where

p, T = [Nm^{-2}, K]

p_0, T_0 = pressure, temperature at normal conditions [101,325 Nm^{-2}, 273.15 K]

For tube dischargers, the corona start potential can be calculated with equation (3):

$$U_0 = r_0 \cdot E_0 \cdot \ln \frac{R}{r_0} \tag{3}$$

Where

U_0 = corona start voltage [V]

R = radius of the tube [m]

For low current densities, the specific corona current I [mA/m] can be calculated for tube dischargers as follows [7]:

$$I = U \cdot 2K \frac{U - U_0}{R^2 \cdot \ln \frac{R}{r_0}} \quad \left[\frac{\sqrt{kg \cdot m}}{s}\right] \tag{4}$$

Where

K = ion mobility [$m^{1.5}\ kg^{-0.5}$]
U = operating voltage [$kg^{0.5}\ m^{0.5}\ s^{-1}$]

The maximum operating voltage U_{max} amounts to a 600- to 800- kV/m spark gap. The breakdown voltage of an electrical discharger depends on several factors. The main parameters are as follows [8]:

- spark gap
- type of electrode
- gas density and composition
- electrical resistance
- power supply system (shape of voltage, frequency)

EXPERIMENTAL SETUP

Figure 1 shows the experimental setup of the NO oxidation process. A thin electrode was built concentrically in an alumina tube and prestressed with a spiral spring. The electrode was connected to the high-voltage device, and the alumina tube was grounded. Due to the poisonous nature of the gas, the oxidation reactor was insulated so that it was gastight.

The gas mixtures were produced by mixing air and nitrogen monoxide with electronic flow control valves (model Brooks 5850 E). An intensive mixing was obtained in the mixing chamber (MK). It was possible to use dry or humidified air. Humidified air was produced by saturating dry air in an impinger system (250 mL, porosity 1).

The dilute, optionally humidified NO gas passed the oxidation reactor. Moisture content and temperature were measured at the inlet of the reactor. At the outlet of the reactor, NO and NO_2 were analyzed with a chemiluminescence detector and ozone was measured with an ozone detector (UV absorption).

The power consumption of the reactor was evaluated from voltage measurement at the discharge wire and the voltage drop at the counterelectrode.

Experimental procedure

The gas velocity was controlled with an electronic airflow valve. Nitrogen monoxide was fed to the main stream. The oxidation process was investigated between corona start

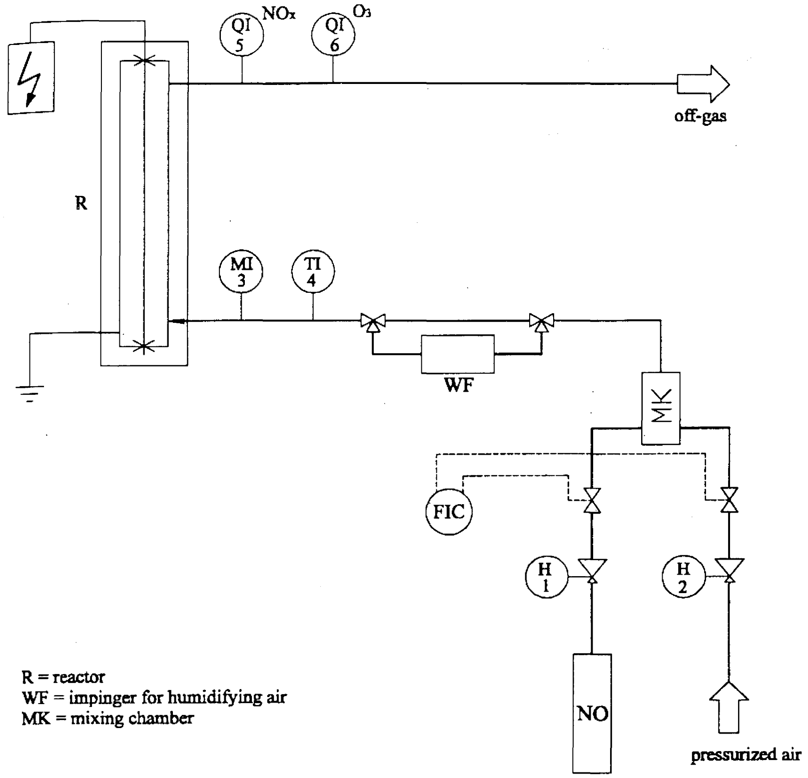


FIGURE 1. Basic flow schema of NO oxidation by corona discharge.

voltage and breakdown voltage. Trends were investigated by raising the voltage in increments of 100 V.

Furthermore, the voltage at the discharge wire and the voltage drop over the counterelectrode were measured for each experiment. The voltage curve and the curve of the voltage drop, which correspond to the corona current, were plotted with an oscilloscope.

The following parameters were varied:

- moisture of the air: $\varphi \approx 10\%$ or $\varphi \approx 100\%$
- NO content: 5, 10, or 15 ppmv

- gas velocity: $v_g \approx 0.3 - 4$ m/s
- voltage device: negative direct current, DC-
  positive direct current, DC+
  alternate current, AC (50 Hz)
  high-frequency current, sinus operation
- shape of the electrode.

The shape of the electrode is essential for the production of ozone. For testing different electrode shapes two reactors were built (Figures 2 and 3). Several profiles were tested in reactor 1:

- ♦ tungsten wire, 0.3-mm diameter
- ♦ form of thread, metric M 2 made of brass
- ♦ different profiles made of brass (Figure 4)
  - * H-profile
  - * Square-profile
  - * L-profile
  - * T-profile
- ♦ The profile used in reactor 2 consists of a brush discharge electrode.

For total specification of the absorption process, the power consumption was measured. The high-voltage measurement was carried out with an oscilloscope (Tektronix Tek Scope THS 710 and probe Tektronix P 6015 A, ratio 1000:1). The current was measured via evaluation of the voltage drop at a defined resistance (Figure 5). The voltage drop was measured with a multimeter (Fluke 8060A Digital True RMS multimeter) and calculated by equation (5):

$$\Delta U = \sqrt{\Delta U_{DC}{}^2 + \Delta U_{AC}{}^2} \tag{5}$$

The current was then calculated with Ohm´s law:

$$I = \frac{\Delta U}{R} \tag{6}$$

To calculate the power consumption of the oxidation reactor, information concerning the phase-shift angle was necessary. The current curves and voltage curves derived from the oscilloscope plot (Figures 6 and 7) permitted the determination of the phase-shift angle to

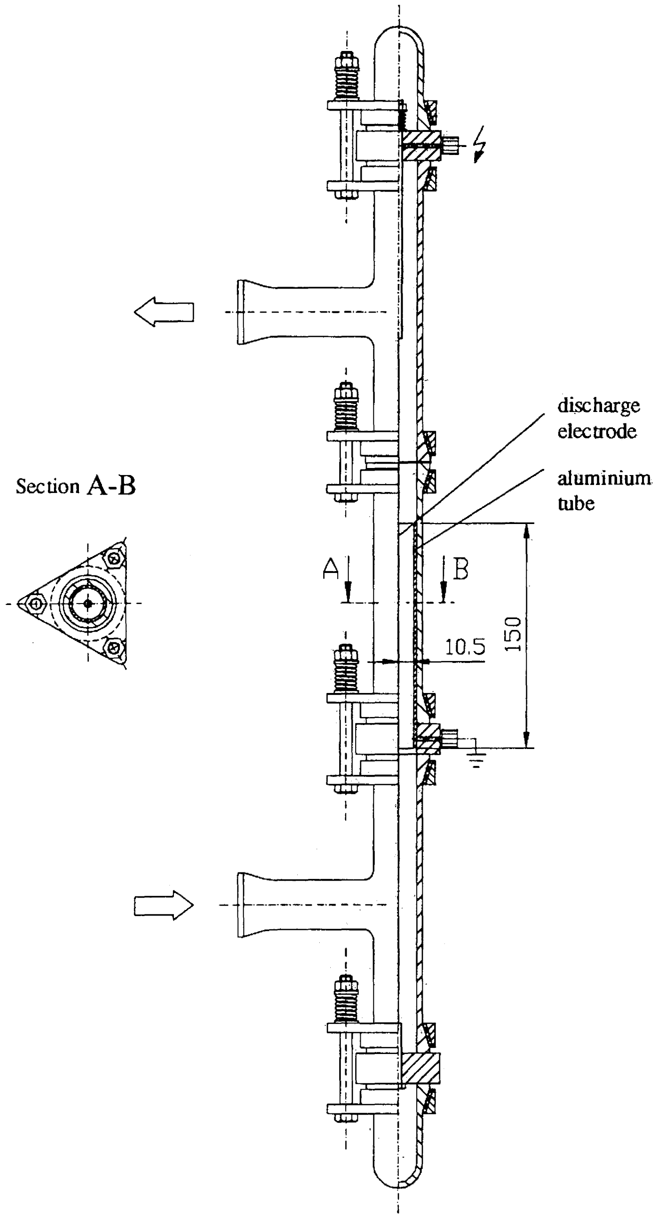


FIGURE 2. Detailed drawing of the oxidation reactor 1.

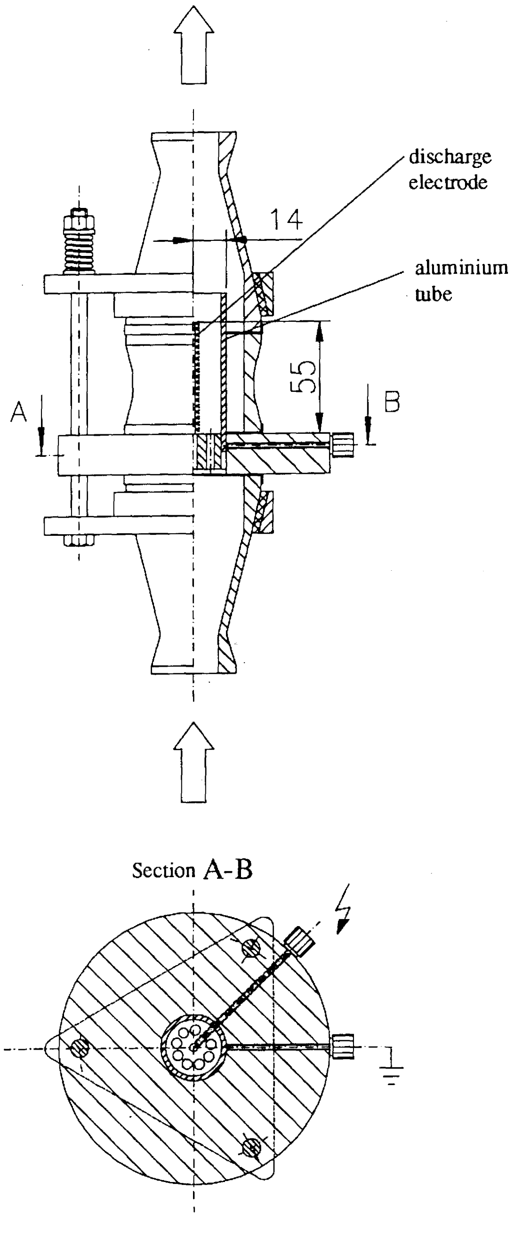
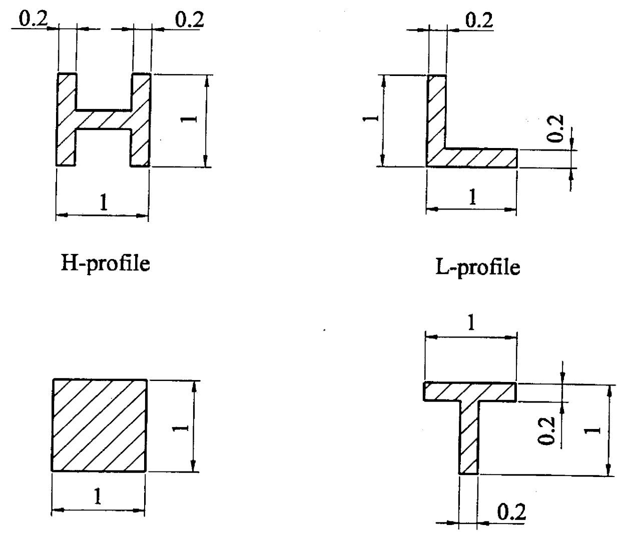


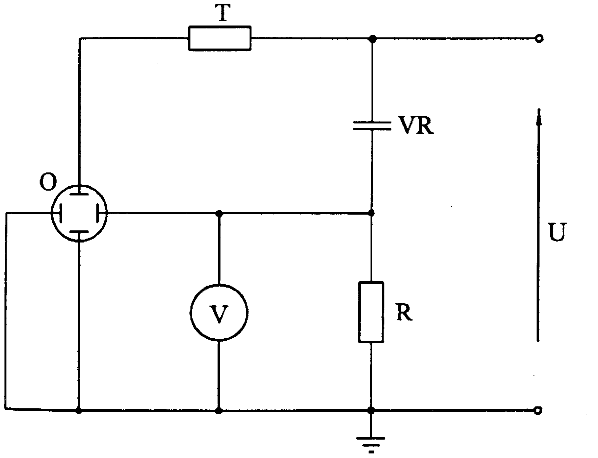
FIGURE 3. Detailed view of reactor 2.



H-profile L-profile

Square-profile T-profile

FIGURE 4. Profiles used for investigation of NO oxidation (dimension: mmscale)



O = oscilloscope
R = electrical resistance (100 Ohms)
T = probe (1000 : 1)
U = high-voltage device
V = voltmeter
VR = reactor

FIGURE 5. Device for the measurement of the electrical power consumption

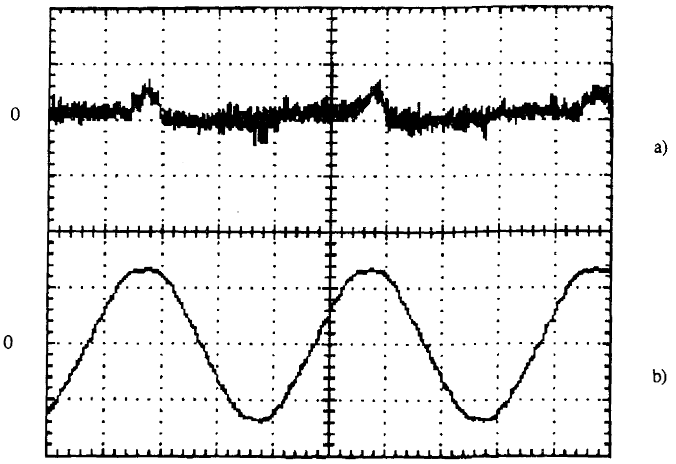


FIGURE 6. Curve of the corona current and the voltage versus time at the corona starting voltage, axis = 5-ms/scale, NO content = 15 ppmv at the reactor entrance, gas velocity $v_g = 1$ m/s:

(a) corona current axis = 0.1-mAscale,

(b) high voltage axis = 5-kVscale (Ueff = 4.8 kV, f = 50 Hz).

be zero, straight from the beginning of the corona start voltage when applying an AC corona for oxidation of NO. The power consumption was then calculated by equation (7):

$$P = U \cdot I \tag{7}$$

The calculation of the nitrogen monoxide flow was derived from equation (8):

$$NO\left[\frac{\text{mmol}}{\text{h}}\right] = \frac{\dot{V}\left[\frac{\text{m}^3}{\text{h}}\right] \cdot NO\,[\text{ppmv}] \cdot p[\text{Pa}]}{R\left[\frac{\text{J}}{\text{kmol} \cdot \text{K}}\right] \cdot T[\text{K}]} \tag{8}$$

Where

NO [mmol/h] = low rate of nitrogen monoxide

p [Pa] = system pressure

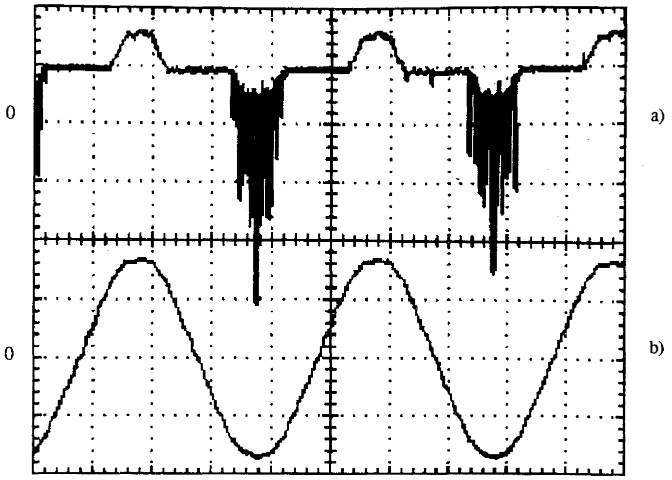


FIGURE 7. Curve of corona current and high voltage versus time during elevated corona discharge conditions, axis = 5-msscale, NO content = 15 ppmv as reactor input condition, 1-m/s gas velocity:

(a) corona current axis = 0.5-mAscale,

(b) high voltage axis = 5-kVscale (Ueff = 6 kV, f = 50 Hz).

The rate of nitrogen monoxide conversion is defined with equation (9):

$$AG_{NO}[\%]=\frac{\Delta NO}{NO_0}\cdot 100 \qquad (9)$$

Where

ΔNO [mmol/h] oxidated amount of nitrogen monoxide

The specific energy consumption for the oxidation of nitrogen monoxide can be calculated with equation (10) (an equimolar conversion of nitrogen and ozone is assumed):

$$E_{NO}\left[\frac{KWh}{kg_{O_3}}\right]=\frac{P[W]\cdot 1000}{\Delta NO\left[\frac{mmol}{h}\right]\cdot 48\left[\frac{mg}{mmol}\right]} \qquad (10)$$

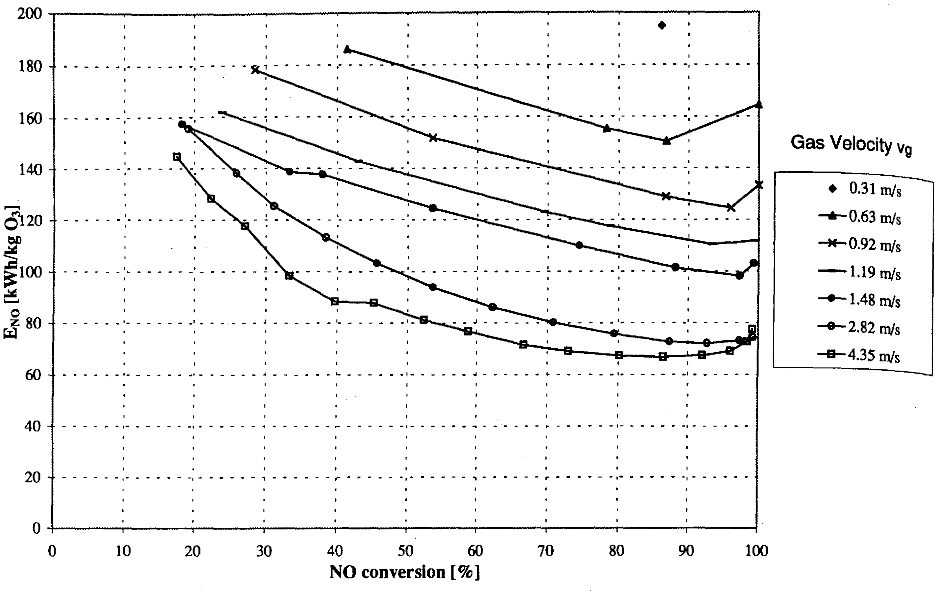


FIGURE 8. Specific energy consumption for the oxidation of NO with negative DC discharge; operating conditions: tungsten wire; 0.3-mm diameter; 15-ppmv NO inlet content; dry waste gas

RESULTS AND DISCUSSION

The objective of the project was the investigation of the specific energy consumption for the oxidation of dilute nitrogen monoxide in waste gas. Different parameters, such as moisture, NO content, gas velocity, voltage device, and shape of the discharge electrode, were varied. All experiments were carried out at ambient temperature and pressure.

The project started with the investigation of the influence of moisture content on the rate of NO oxidation when using a tungsten discharge electrode. The process parameters gas velocity and voltage device were varied.

The lowest specific energy consumption was obtained when negative direct-current (DC) corona was applied. The specific energy consumption increased in series in which negative DC, alternate current (AC), positive DC and high frequency current with sinus

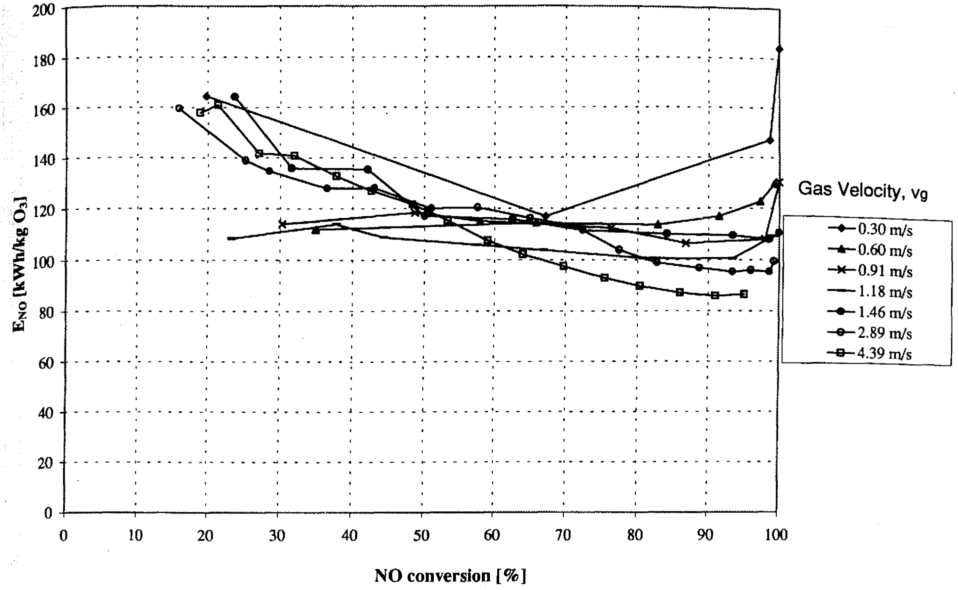


FIGURE 9. Specific energy consumption for the oxidation of NO with with negativ DC-discharge; operating conditions: tungsten wire; 0.3 mm diameter;15 ppmv NO-inlet content; water-saturated waste-gas

operation were applied. Figure 8 shows the rate dependency of the specific energy consumption when applying negative DC corona and dry, dilute waste gas.

The specific energy consumption decreased with increasing gas velocity. This trend can be explained by the velocity dependency of the voltage-current characteristic [9]. A minimum in specific energy consumption was observed at an oxidation rate of approximately 95% of the nitrogen monoxide.

In comparison to the properties of dry waste gas, Figure 9 shows the specific energy consumption when waste gas saturated with water was investigated.

In general, water-saturated gas required 20 - 30% more energy than dry gas. Further investigations were therefore carried out with water-saturated waste gas, as these off-gas conditions are more common in technical applications. In this case, humidificaton of the gas is greater than 50%. The oxidation rate of the corona discharge process depends

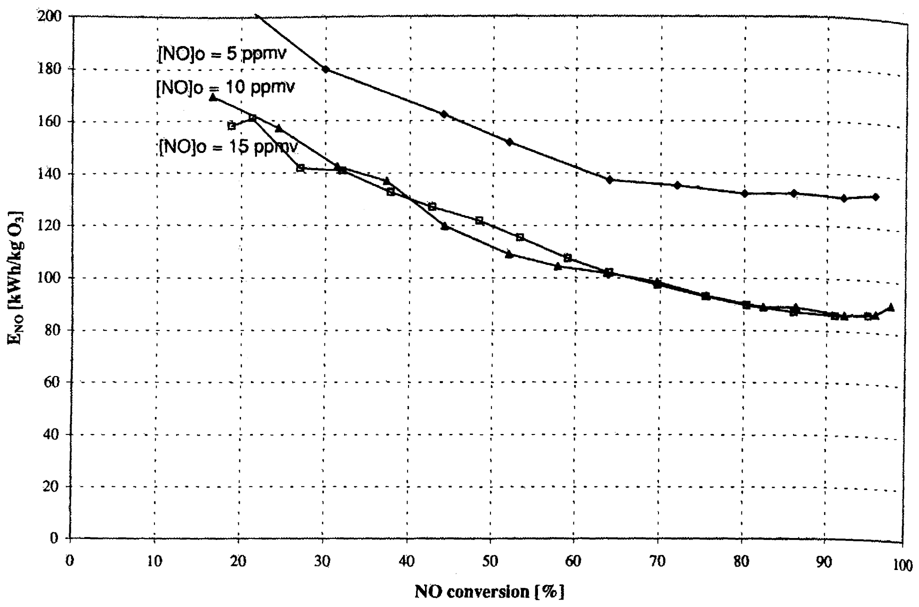


FIGURE 10. Specific energy consumption for the oxidation of NO with negative DC discharge; operating conditions: tungsten wire, 0.3-mm diameter; water-saturated waste gas; gas velocity $v_g = 4$ m/s.

strongly on the content of nitrogen monoxide. A decrease in the nitrogen monoxide content from 15 to 5 ppmv resulted in 30% more specific energy consumption (Figure 10). This indication is of technical significance, as tunnel off-gas normally contains 5 ppmv NO and about 1 ppmv NO_2.

Figure 11 shows the formation of excess ozone in the off-gas. The excess ozone is related to the NO content of the feed. With decreasing NO content of the feed,excess ozone was detected at lower conversion levels of NO. Based on equation (10), this behavior explains the minimum in specific energy consumption.

After investigation of the main parameters (voltage, gas velocity, and NO content) further experiments focused on the shape of the electrode.

The lowest specific energy consumption (60 KWh/kg O_3) was obtained with L- and T-profiles applying negative DC discharge, water-saturated inlet gas, and an NO content of

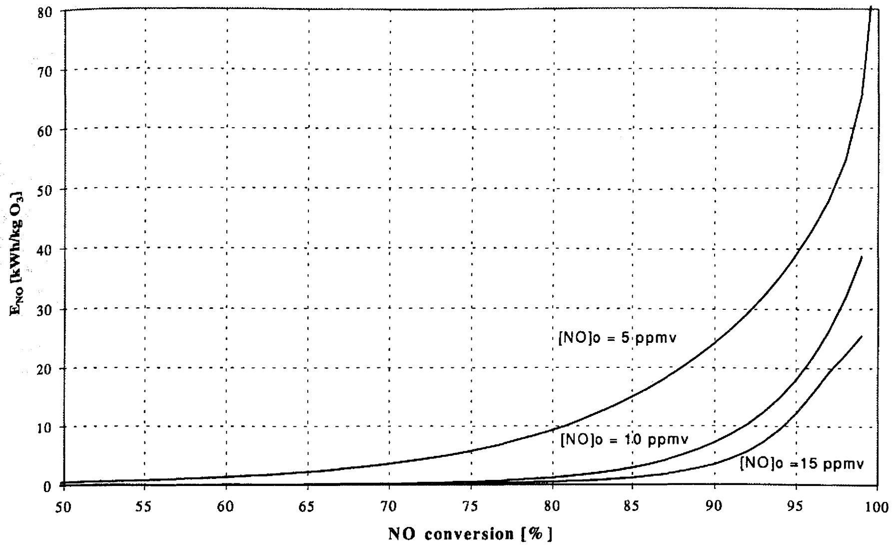


FIGURE 11. Formation of excess ozone in off-gas when applying negative corona discharge with different NO content: tungsten wire, water-saturated waste-gas, gas velocity $v_g = 1.1$ m/s.

15 ppmv (Figure 12). In comparison with the results achieved with the tungsten discharge electrode, investigations with the geometric shapes (H-profile, square-profile and metric thread M2) resulted in higher specific energy consumption.

Furthermore, the specific energy consumption for waste gas with an NO content of 5 ppmv was measured to be 70 - 90 KWh/kg O_3 with L- and T-profiles.

Experiments with the brush discharge electrode led to a specific energy consumption comparable with that of the H-profile.

SUMMARY

The objective of this project was the investigation of direct corona discharge oxidation of NO under different operating conditions (moisture, NO content, gas velocity, voltage

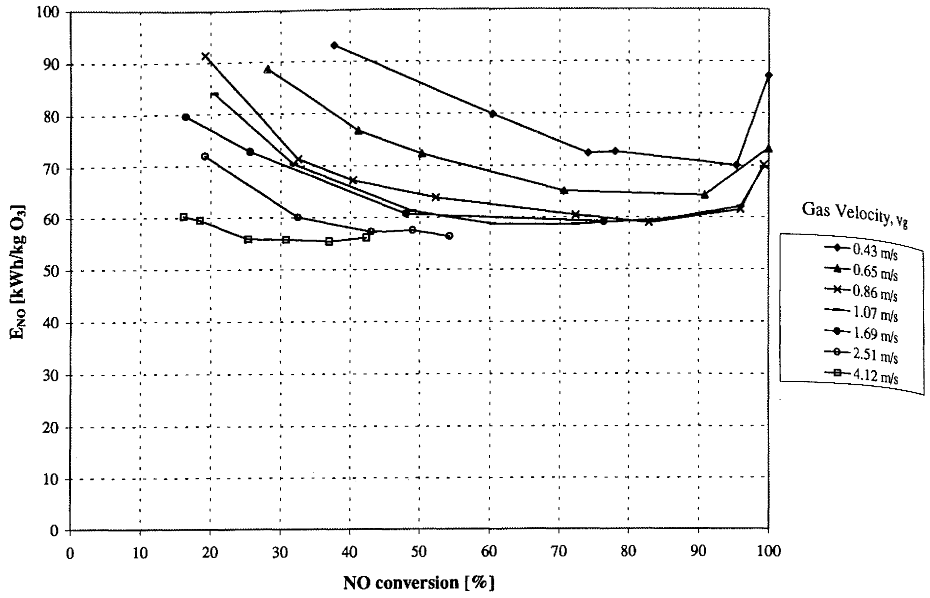


FIGURE 12. Specific energy consumption for the oxidation of NO with negative DC discharge; operating conditions: T-profile; water-saturated waste gas; 15-ppmv NO content.

device, and shape of discharge electrode). Trends and the minimum energy consumption for oxidation were evaluated.

With regard to the application of the technique in tunnel off-gas purification, the experiments were carried out in tube reactors at ambient temperature and pressure.

The project started with the investigation of the influence of the moisture content when using a tungsten discharge electrode and negative DC discharge.

In general, water-saturated waste gas requires 20 - 30% more energy than dry gas. The energy demand decreases with increasing gas velocity. The lowest specific energy consumption was obtained when negative DC current was applied. Furthermore, an increase in the specific power consumption was detected when the NO-content of the feed gas decreased. However, the minimum specific energy consumption was evaluated to be 130 KWh/kg O_3 when the operating conditions were comparable with the technical application.

The formation of ozone during the oxidation of nitrogen monoxide was also measured. An increase of ozone formation was obtained with decreasing initial NO content.

Further experiments focused on the shape of the discharge electrode. In comparison to the results obtained with the tungsten discharge electrode the lowest power consumption (70 - 90 KWh/kg O_3) was measured when applying L- and T-profiles.

Excluding the effect of particle separation by application of direct corona discharge for the oxidation of NO in dilute off-gas, the specific energy consumption will not meet economic requirements.

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