NITROGEN OXIDES SYNTHESIS IN A D.C. PLASMA JET

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ABSTRACT

Nitrogen oxides was performed in a free nitrogen-oxygen plasma jet at atmospheric pressure. Electrical power was from 5 up to 30 kW and each gaz flow rate was from 10 up to 100 Nl/mn.

The influences of nitrogen molar fraction, reactor pressure, cold wall quenching, nozzle design, on synthesis efficiency have been investigated.

Numeric simulation of plasma chemical kinetics was computed in order to point out the influence of temperature history on the conversion rate.

1. INTRODUCTION

The numerous papers on nitrogen oxides synthesis submitted to the last Symposium on Plasma Chemistry have pointed out this research field actuality ; the plasma devices were so different as microwave plasma /1/, /2/, R.F. plasma /3/, low /4/ and high /5/ /6/ intensity arc plasma, and glow discharges /7/.

Our improved experimental set-up /6/ allows working conditions with up to 50 % of oxygen in the plasma gas mixture.

Starting from an equimolar nitrogen-oxygen mixture, we have carried out systematic experiments under atmospheric pressure. The NO_2 molar fraction was up to 10 % in the final products whereas the maximum predicted value from C.L.T.E. calculations is about 6.7 % at 3 500 K. In order to explain this deviation from equilibrium composition, we have elaborated a theoretical model involving chemical kinetics.

2. EXPERIMENTAL SET-UP

All the devices are described in details in /8/. The plasma gas-mixture - nitrogen and oxygen - is introduced along the cathode , oxygen is cold injected downstream the arc into the nozzle and so contributes to the quenching which is completely achieved by removing the gaseous products through a water cooled probe.

The plasma torch and the quenching probe are placed on the axis of a water cooled double wall vessel equipped with two windows for spectroscopy diagnostics. This reaction vessel is pressurised for the atmosphere and pressure controls.

A part of the quenched gases is removed through an absorption tube for optical measurement of NO_2 partial pressure.

The ranges of the different working parameters are :

60 and 260 A	for the arc current intensity
9 and 70 Nl/mn	for the nitrogen flow rate in the arc
8 and 30 Nl/mn	for the oxygen flow rate in the arc
10 and 110 Nl/mn	for the oxygen flow rate in the nozzle
1 and 2 bars	for the pressure in the reaction chamber
60 and 130 V	for the arc voltage
5 and 27.2 kW	for the electrical power

The plasma torch efficiency ρ defined by $((P_{el}-P_Q)/P_{el})$ was about 75 % : P_{el} is the electrical power supplied and P_Q is power lost in torch cooling water.

Specific enthalpy - energy provided to plasma gas unit mass - was from 1.4 up to 7.7 kWh/kg.

Gas flow velocity at the nozzle exit, measured without oxygen injection, was between 500 and 1000 m/s.

3. EXPERIMENTAL RESULTS

We have pointed out that :
- energetic consumption presents a minimal value with an initial nitrogen molar fraction about 50 % /6/
- NO_2 molar fraction decreases with the initial nitrogen molar fraction X_{N_2} (figure 1)
- NO_2 molar fraction increases with the pressure in reaction chamber (figure 2)
- cold wall quenching device has allowed us to increase NO_2 molar fraction as to reduce energetic consumption /9/
- nozzle must be long enough to prevent arc foot to stay downstream the cold oxygen injection /9/.

The result shown on figure 3 have been selected among the lot of results we have obtained ; versus specific enthalpy H we have plotted : the NO_2 molar fraction y_{NO_2}, the fixed nitrogen rate α, the energetic consumption C, and the energetic conversion efficiency η (ratio of the NO molar binding energy - 90 kJ/mole - on the electrical energy consumed for the synthesis of one NO mole).

4. CHEMICAL KINETICS MODEL

The final products, after quenching, have a concentration higher than the maximum predicted by equilibrium calculations at the same pressure. Departure from equilibrium can be partialy explained by chemical kinetics considerations : quenching models from high temperature equilibrium have been proposed by Polak /10/ from /11/ and /12/ and by Amman /13/.

4.1 Computing method

Let us consider a mixture of I chemical species A_i reacting in J chemical reactions with reaction rate constants k_j :

$$(1) \quad \sum_{i=1}^{I} \nu_{ji} A_i \xrightarrow{k_j} \sum_{i=1}^{I} \nu'_{ji} A_i$$

The thermodynamic temperature of the system is assigned to follow a law $T = f(t)$ which is supposed to describe the temperature history of the bulk gaz from entrance of the torch to the end of the reactor. The pressure is assumed to be constant all along the system.

If diffusion processes are neglected the time dependence of the chemical composition of the system is calculated by solving the following differential sytem.

$$(2) \quad \frac{dy_i}{dt} = w_i - \left(\frac{y_i}{\rho} \sum_{i=1}^{I} w_i + \frac{y_i}{T}\frac{dT}{dt}\right)$$

where y_i is the molar concentration of the i^{th} specie , $\rho = P/kT$ and w_i the production and loss terms for i^{th} specie.

$$(3) \quad w_i = \sum_{j=1}^{J} k_j (\nu'_{ji} - \nu_{ji}) \prod_{l=1}^{I} y_l^{\nu_{jl}}$$

If the initial concentration $y_i(0)$ are known, the differential system can be solved using the appropriate predictor-corrector method proposed by Winslow /14/.

4.2 Reactions and reaction rate constants

We have used data gathered by Prud'Homme /15/, and these recommended by Baulch /16/.

At temperature below 5000 K only the following neutral species have been considered : N_2, O_2, NO, N and O. They are supposed to take part in the following reactions

(4) $O_2 + M \rightleftarrows O + O + M$ (5) $N_2 + M \rightleftarrows N + N + M$

(6) $NO + M \rightleftarrows N + O + M$ (7) $O_2 + N_2 \rightleftarrows NO + NO$

(8) $O + N_2 \rightleftarrows NO + N$ (9) $N + O_2 \rightleftarrows NO + O$

The selected rate constants are listed in Table 1. M is any one of the five species.

4.3 Results

From some measurements performed on a nitrogen-oxygen plasma jet we have fitted the experimental time-temperature history along the reactor in the following manner. The temperature at each end of the reactor is 300 K, the gas is heated up to 5000 K in 10^{-5} sec. The initial value of the heating rate (dT/dt) is 10^9 K/s, its mean value is 5 10^8 K/s, the heating law is parabolic with time. A similar parabolic law is used for the quenching step during 9 10^{-5} s with an initial rate - 10^8 K/sec.

Molar fractions versus time are shown in figure 4. Figures 5, 6 and 7 describe respectively the time evolution of the over all production of NO (d(NO)/dt), N and O and the production of NO, N and O by each of the reactions (4) to (9).

At the very beginning of the reaction ($t < 5$ µsec, $T < 4000$ K) the production of NO is due mainly to reaction (7), a result which is not in agreement with the conclusions of Zel'Dovich /11/ and Polak /10/ for this process. At the same time N is produced by reaction (8).

The maximum production rate of NO is reached between 8 and 12 µsec

(T = 4000 ↑ 5000 ↓ 4800 K) and processes (7) (8) and (9) produce an equivalent amount of NO. The production rate of N by process (8) is equal to the loss rate by process (9) and (N) is maximum. Between 12 and 18 µsec (T = 4800 ↓ 4200 K) the processes (7) (8) and (9) always produce NO but with a lower rate until a zero rate is reached at 18 µsec and the process (9) destroy N.

Between 18 and 60 µsec (T = 4200 K ↓ 1500 K) reactions (8) and (9) slightly destroy NO. The destruction of N by the process (9) is higher than the production by (8).

From t = 60 µsec (T < 1500 K) the system is partially frozen especially for NO since there is no more atomic nitrogen and oxygen recombines very slowly by the process (4) which governs (O) during the total reaction time.

Processes (5) and (6) are significant only at high temperature (T > 4500 K).

5. CONCLUSION

At 1 atm. the frozen high temperature equilibrium predicts a maximum of (NO) of 7 %, the kinetics model shows that it is possible to obtain up to 11 % (a result which is in good agreement with experiment).

The important role of quenching rate is shown with our model, but, as far as we know, it is the only one which points out the equally important role of heating rate. The heating rate controls the maximum concentration of NO as the quenching controls the freezing of the high temperature mixture.

Moreover chemical kinetics model shows that gas enthalpy may be recovered since 2000 K. With a simplified process schema involving energy recycling, we have shown that an electrical energy consumption as low as 7 kWh/kg NO may be expected. So the electrical synthesis process should be competitive compared with the classical one.

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	B	α	E
(4)d	$3.2\ 10^{19}$	-1	118000
(4)r	$5\ 10^{15}$	-.25	0
(5)d	$4.1\ 10^{22}$	-1.5	224900
(5)r	$1.2\ 10^{17}$	-.5	0
(6)d	$2.9\ 10^{19}$	-1.	150000
(6)r	$4.3\ 10^{20}$	-1.5	0

	B	α	E
(7)d	$9.1\ 10^{24}$	-2.5	128500
(7)r	$2.4\ 10^{23}$	-2.5	85500
(8)d	$7.\ 10^{13}$	0	75500
(8)r	$1.3\ 10^{11}$	0.5	0
(9)d	$1.\ 10^{11}$	0.5	6200
(9)r	$2.0\ 10^{10}$	0.5	38400

Table 1 - Reaction rate constants: $k=B\ T^{\alpha}\ \exp(-E/RT)$

$E(cal.mole^{-1})$

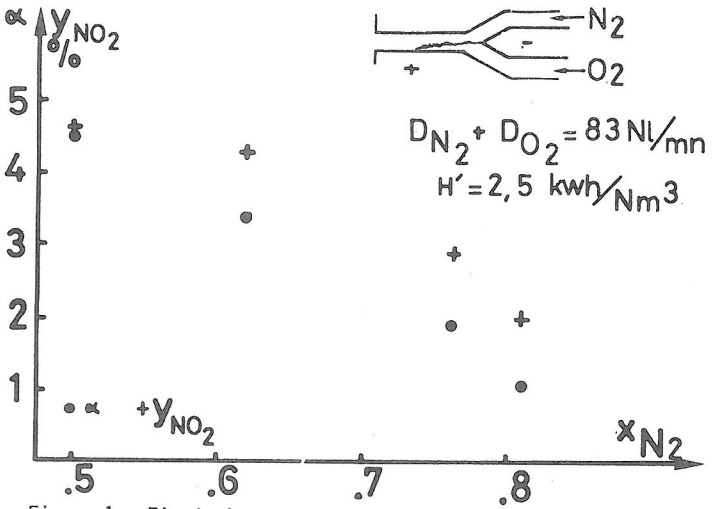

Figure 1 - Fixed nitrogen rate and NO_2 molar fraction y_{NO_2} versus N_2 initial molar fraction.

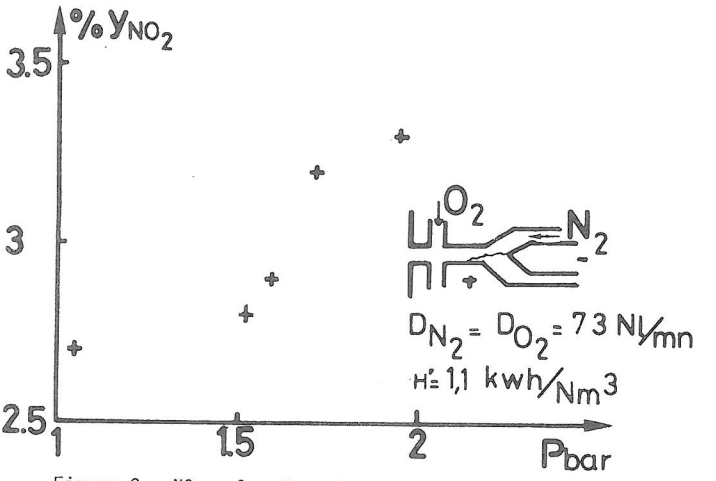

Figure 2 - NO_2 molar fraction versus pressure.

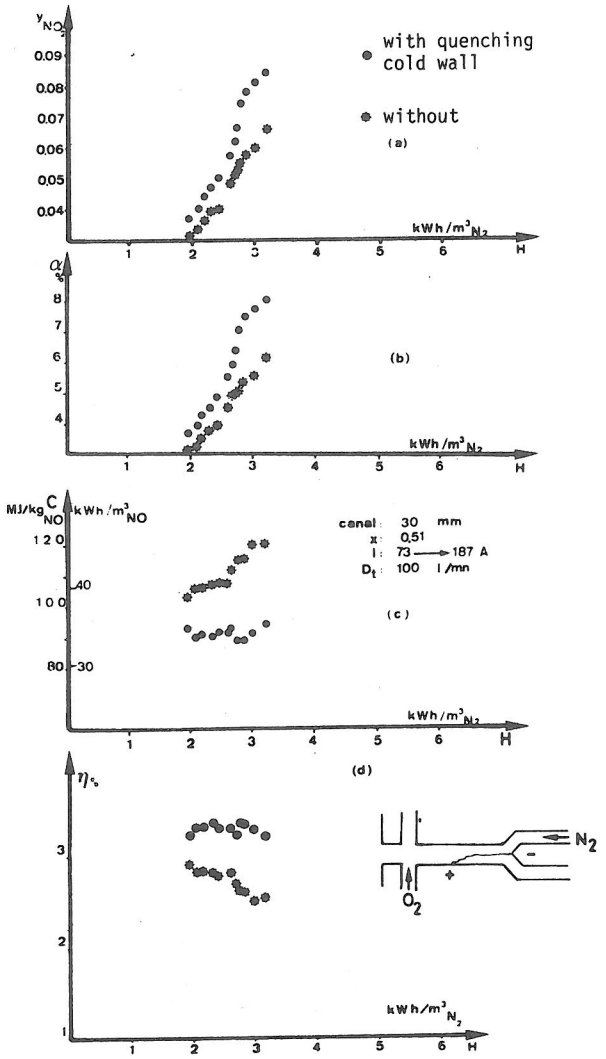
with quenching cold wall
without
(a)
(b)
(c)
(d)
canal : 30 mm
x : 0,51
I : 73 → 187 A
D_t : 100 l/mn
kWh/m³ N_2
MJ/kg NO
kWh/m³ NO
N_2
O_2

Figure 3

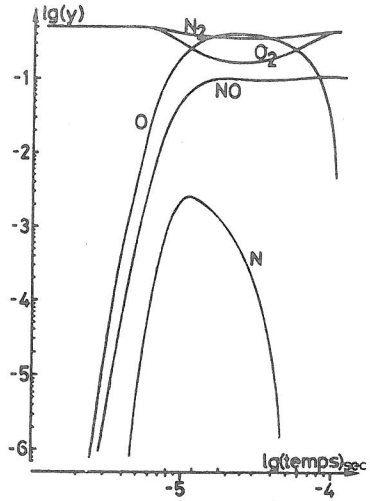

Figure 4 - Molar fraction versus time.

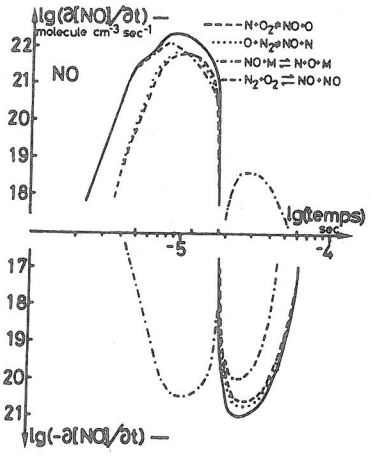

Figure 5 - NO production rate versus time.

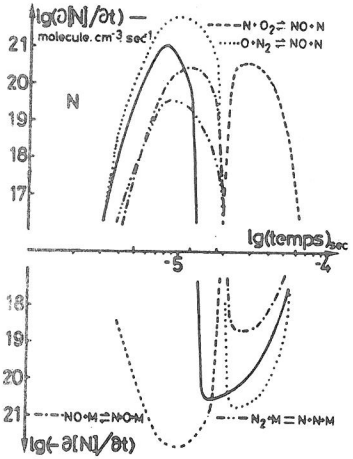

Figure 6 - N production rate versus time.

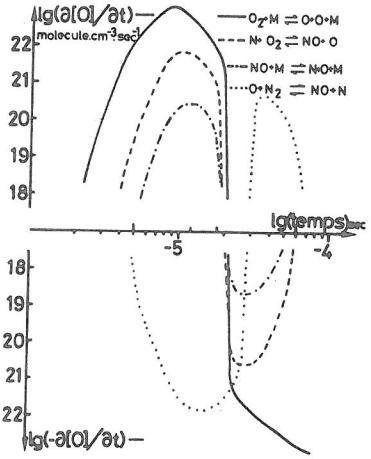

Figure 7 - O production rate versus time.