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Energy cost improvement of the nitrogen oxides synthesis in a low pressure plasma

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Abstract. — Nitrogen oxide is synthesized from a N₂-35 % O₂ mixture flowing (22 Nl/h) through a microwave discharge. The total pressure is equal to 50 torr. The optimal value of energy consumption, equal to 28 MJ/kg NO, is obtained with catalyst such as MoO₃. Results are improved by 53 % in comparison with the industrial process used at present, and by 78 % in comparison with those obtained with a plasma jet arc generator.

1. Introduction.

Industrial synthesis of nitric acid is achieved by catalytic oxidation of NH₃ to NO and NO₂. This reaction, similar to a combustion, produces energy which can be recovered. But, in spite of considerable improvement in this field, the energy consumption of a unit of production of nitric acid remains excessive, and in the best conditions, the production of nitrogen oxides takes 60 MJ/kg NO, with a mole concentration of NO equal to 8 % in the gaseous flow [1]. This absolute efficiency remains rather poor. Thermodynamic calculations show that the formation of NO from the reaction:

\[ \text{N}_2 + \text{O}_2 \rightarrow 2 \text{NO} \]  

(1.1)

requires 10 MJ/kg NO in the hypothetical case of a strong thermodynamic non-equilibrium favorable to the NO formation. Within this hypothesis, the maximum energy yield would be 30 % [2].

As early as the end of XIXth century, the synthesis of nitrogen oxides by an electric discharge through the air has been proposed, but poor yields caused it to be abandoned. However, for the past five years, the use of electric energy for this synthesis has been the object of new research.

By means of a direct current plasma jet of N₂ at atmospheric pressure with O₂ injected, J. F. Coudert et al. [3] obtained a 6.5 % nitrogen oxidation rate for an energy consumption of 120 MJ/kg NO. Using air as plasma gas in a furnace, I. Pollo [4] obtained 4.75 % NO. The main problems of this technique is the quenching of NO. The re-dissociation of NO caused by the high temperature of the system does not give any hope for improvement in the result. J. Amouroux et al. [5] studied the NO₃ formation in a plasma by induction, first of all for low pressures. By substituting a coating of MoO₃ or WO₃ for pyrex wall, the fixation rate of nitrogen on oxygen increases from 8 to 19 % [6] for pressures ranging from 3.75 to 30 torr. By means of a lateral injection of the plasma into a fluidised bed [7], they transpose the low pressure catalysis to high pressures. The volume of nitrogen oxides produced is then 2.8 %.

From thermodynamic calculations [2], it is shown that vibrationally excited ground electronic state nitrogen molecule \( \text{N}_2(\text{X}_v) \) is involved in the nitrogen oxides synthesis according to the reaction:

\[ \text{N}_2(\text{X}_v) + \text{O}(^{3}\text{P}) \rightarrow \text{NO} + \text{N} \]  

(1.2)

The equilibrium value of the vibrational temperature \( T_v \) is determined: \( T_v = 0.4 \text{ eV} \).

Our previous work [8] in fundamental chemical
kinetics gives evidence for the importance of the heterogeneous reactivity of \( \text{N}_2(X) \) in thermodynamic non-equilibrium plasma obtained by a microwave discharge through nitrogen. This result supports the hypothesis that \( \text{N}_2(X) \) is the molecule responsible for \( \text{NO}_x \) synthesis according to:

\[
\text{N}_2(X)_{\text{ads}} + \text{O}_{\text{ads}} \rightarrow \text{NO} + \text{N}.
\] (1.3)

These observations have led us, first of all, to determine the nitrogen pressure \( (p_{\text{N}_2}) \) compatible with the higher possible \( \text{N}_2(X) \) concentration \( \{\text{N}_2(X)\}_j \) so as to optimize reaction (1.3), and then to improve the yield of this reaction with the use of a catalyst.

Direct experimental evidence for the existence of \( \text{N}_2(X) \) in active nitrogen afterglow has been shown by pulsed multichannel laser Raman spectroscopy [9]. This method makes possible a spatial and temporal study of the population of the vibrational levels. Figure 1 shows the Raman spectrum of \( \text{N}_2(X) \), which has been obtained for an active nitrogen pressure equal to 20 torr. Vibrational levels up to 5 are undoubtedly obtained. Vibrational temperature and steady concentrations of \( \text{N}_2(X) \) in the gaseous flow are evaluated versus \( p_{\text{N}_2} \) and the flow time \( (t) \) between the discharge and the observation zone. \( \{\text{N}_2(X)\}_j \) decreases when the pressure increases (Table I). The higher nitrogen pressure compatible with a noticeable \( \{\text{N}_2(X)\}_j \) is equal to 40 torr. So, all the studies about nitrogen oxides synthesis are carried out under this pressure condition which corresponds to a flow rate equal to 18 Nl/h.

<table>
<thead>
<tr>
<th>( p_{\text{N}_2} ) (torr)</th>
<th>18</th>
<th>23</th>
<th>31</th>
<th>38</th>
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</thead>
<tbody>
<tr>
<td>10</td>
<td>32 ± 4</td>
<td>35 ± 4</td>
<td>24 ± 3</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>34 ± 4</td>
<td>36 ± 5</td>
<td>29 ± 4</td>
<td>28 ± 4</td>
</tr>
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<td>31 ± 4</td>
<td>27 ± 4</td>
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</tr>
<tr>
<td>70</td>
<td>19 ± 2</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

### Table I. — Percentage of \( \{\text{N}_2(X)\}_j \) versus \( p_{\text{N}_2} \) and the flow time \( (t) \) between the discharge and the observation zone.

2. Experimental device.

The experimental apparatus (Fig. 2) used for the direct synthesis of nitrogen oxides has been described previously [10]. The gaseous flow, created by a continuous pumping, is excited in an electrodeless discharge by means of a microwave generator GHF 1211 C Thomson-CSF (frequency 2450 ± 50 MHz) which is a wattmeter allowing the measurement of the incident \( (P_i) \) and reflected \( (P_r) \) power. Studies are carried out in the optimum adaptation condition corresponding to \( P_r = 0 \). The discharge cavity, conceived and built in the laboratory, has been previously described [11].

![Diagram of the experimental setup](image)

The reactor, a quartz tube with 15 mm inner diameter, is cooled with compressed air. The two reactive gases (\( \text{N}_2 \) and \( \text{O}_2 \) Air Liquid quality) are injected together upstream from the discharge. Pressure is measured near the discharge zone. \( p_{\text{N}_2} \) is constant and equal to 40 torr. The nitrogen oxides produced are trapped in liquid nitrogen and the conversion of \( \text{N}_2 \) into these oxides are determined by acidimetric titration [12].
Catalytic reactions are studied with MoO$_3$. This oxide is prepared in the reactor by the combustion of a Mo wire (diameter = 0.25 mm) in an active oxygen flow ($p_{O_2} = 100$ torr). This catalyst is situated just down-stream from the discharge: first of all we wanted to obtain the lowest possible temperature of the catalyst (to avoid the formation of metallic vapour) and then to create the possibility for oxygen atoms or excited oxygen molecules with short lifetimes to regenerate the catalyst. However, its efficiency decreases quickly, and an efficient regeneration is obtained with a molecular oxygen flow. On the other hand, when the catalyst is situated in the discharge, the excitation of the gaseous flow requires an energy too high (within 200 W) to be involved in our system: such a use of the catalyst would lead to an increase of the energy consumption.

3. Experimental results.

The measurement of the energy provided to the plasma gas enable to convert results into energy consumption by unity of mass of NO$_x$.

The use of gaseous mixtures with a O$_2$ content ranging from 29 % to 43 % allows to determine that without catalyst the 35 % mixture gives the best result, whatever the power may be (Fig. 3). The total pressure is then equal to 50 torr, and the total gaseous flow is 22 Nl/h. Figure 1 shows that the energy consumption decreases with the microwave power. For a N$_2$-35 % O$_2$ mixture, the lowest possible operating power value is 10 watt. The energy consumption in such conditions is equal to 43 MJ/kg NO, and the reproducibility of the results is about 2 %. The mole concentration of nitrogen oxides in the gaseous flow is 4 %.

With catalyst, figure 4 shows that $x_{O_2} = 0.47$ is the lowest O$_2$ mole fraction giving the lowest energy consumption. The total pressure corresponding to a N$_2$-47 % O$_2$ mixture is equal to 60 torr, and the lowest possible operating power value is 60 W. In these conditions, the energy consumption doesn’t varie versus the « age » of the catalyst. On the other hand, with low O$_2$ mole fraction, the efficiency of the catalyst decreases with time. An efficient regeneration is obtained with a molecular oxygen flow. In order to compare with the value obtained without catalyst, the energy consumption is measured for a N$_2$-35 % O$_2$ mixture and a power equal to 10 W. In these conditions the energy cost is equal to 28 MJ/kg NO corresponding to an improvement of 35 % in comparison with the results obtained without the catalyst [10]. The mole concentration of nitrogen oxides in the total gaseous flow in then 6 %.

As it has already been shown [4], it is not possible, in a single experiment, to obtain both the maximum concentration of nitrogen oxides and the minimum energy cost.

The heterogeneous nature of the reaction can also be shown by increasing the surface/volume ratio of the reactor, for instance with quartz wool which has a very high specific area. This method improves the energy cost by 11 %.

4. Conclusion.

Energy consumption for nitrogen oxides synthesis is improved by 53 % in comparison with the industrial
process used at present, and by 78% in comparison
with those obtained with a plasma jet arc generator.
It should be possible to obtain a best energy cost by
increasing the specific catalytic surface, or by returning
the discharge products back into the discharge as it
has already been suggested by Alamavo and Hod-
Hasharon [13].
In our system, the nitrogen oxides synthesis occurs in
thermodynamic non-equilibrium. Thus, no quenching
is necessary to obtain NO₃. This is an advantage in
comparison with other methods in high temperature
plasma where the quenching is always the main
problem.

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