MODELLING OF NITROGEN OXIDE OXIDATION IN NITRIC ACID PRODUCTION

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ABSTRACT

The paper deals with the problems of mathematical modelling of homogeneous oxidation of nitrogen oxide, which takes place in different parts of nitric acid production plants. Proposed model developments include: 1) algorithm for estimation of model parameters; 2) calculation of nitrous gas composition at the exit of every homogeneous reaction zone; 3) calculation of temperature losses in the tube between the units of the technological scheme.

The developed algorithms are included in software package for the steady-state performance simulation of an absorption column and the whole plant for nitric acid production in the fertilizer production factory in Devnia, Bulgaria.

Keywords: nitric acid, nitrous gas, nitrogen oxide homogeneous oxidation.

INTRODUCTION

The production of diluted nitric acid by the contact method may be expressed by the following chemical reactions [1, 2]:

\[ 4NH_3 + 5O_2 = 4NO + 6H_2O \]  
(1)

\[ 2NO + O_2 = 2NO_2 \]  
(2)

\[ 2NO_2 \leftrightarrow N_2O_4 \]  
(3)

\[ 3NO_2 + H_2O = 2HNO_3 + NO \]  
(4)

A simplified scheme of the dual-pressure nitric acid production in “Agropolichim” – Devnia is shown in Fig.1. It includes: 1) oxidation low-pressure part of the plant, where nitrogen oxides are produced by oxidation of ammonia with atmospheric air over platinum catalyst. The exit stream is cooled at several steps – main boilers, gas-water heat exchangers and in cooler-condensers; 2) in the absorption high-pressure part of the plant the nitrous gas after compression and cooling constitute the feed at the bottom of the absorption column, which receives process water at the top.

Oxidation of NO to NO₂ takes place along the way of gas phase stream and at the entrance of the column the NO conversion has to be about 95 %. At the same time this homogeneous reaction occurs in the gas space between the plates of the absorption column, connected to the produced NO from the synthesis of nitric acid on the plates (see equation (4)).

The nitrous gas is a mixture of several components consisting of N₂O, NO, NO₂, N₂O₃, N₂O₄, N₂O₅. For the conditions of nitric acid production by the contact method is assumed only following gas phase reaction [1, 3]: oxidation of NO; NO₂ dimerisation and N₂O₅ formation from NO and NO₂. Frequently, the last reaction is not taken into account, because the equilibrium concentration for N₂O₅ is very low and rapidly attained. Since reaction (2) is slower than all other homogeneous reactions, it is assumed that only it takes place. For the temperatures below 523K the chemical reaction (2) is irreversible and is expressed by the third order rate equation [4]:

\[ W_{r,NO} = \frac{dp_{NO}}{d\tau} = -0.2166 \exp\left(\frac{1399}{T}\right)p_{NO}^2p_{O_2} \]  
(5)

where: \( p \) is the partial pressure of a component.

Having in mind the possibilities of the other existing homogeneous reaction, many investigators prefer
to express the rate constant as a statistical determined function by experimental data [2]:

\[ k(T) = 50,187 - 0,3627 T + 7,211 \times 10^{-4} T^2 \]  \hspace{1cm} (6)

After integration of the kinetic equation (5), fitting partial pressure to total pressure (using molar part \( \mu \) instead of partial pressure) the next rate equation (7) is obtained [2, 5]:

\[ \tau P^2 k(T) = \frac{1}{(\mu_{\text{in}} - \mu_{\text{NO}})} \left[ \frac{(\mu_{\text{in}} - \mu_{\text{NO}})}{0 - \beta \mu_{\text{NO}}} \ln \frac{1 - \beta}{1 - \frac{\mu_{\text{NO}}}{\mu_{\text{in}}} \beta} \right] \]  \hspace{1cm} (7)

where: \( \beta \) is degree of NO conversion (\( \beta = \frac{G_{\text{NO}}^{\text{in}} - G_{\text{NO}}^{\text{out}}}{G_{\text{NO}}^{\text{in}}} \)), \( G_{\text{NO}}^{\text{in}} \) and \( G_{\text{NO}}^{\text{out}} \) - input and output flow rates of nitric oxide, \( \tau \) - time; \( P \) - total pressure; \( \mu \) - molar part.

Equation (7) gives possibility to calculate the degree of NO conversion \( \beta \) in each reaction zone. In this case instead of \( \tau \), the residence time \( \tau_{av} = V / \nu \) has to be used; the temperature is the average one in the vessel and the pressure \( P \) is the input pressure. \( V \) is the volume of the vessel and \( \nu \) is the volumetric flow rate.

This kinetics has already been applied in an algorithm for modelling the processes in the oxidation part (between the plates) of the absorption column in nitric acid production [6]. The above assumptions are easily proved. For instance, the temperature changes between the plates are up to 7K and this allows to use an iterative established average temperature for the calculation of the rate constant \( k \).

**MODEL DEVELOPMENTS**

**A. Estimation of model parameters**

Homogeneous NO oxidation in the zones where nitrous gas is passing through, have some features:

- the degree of NO conversion and respectively connected with it conditions (concentrations, temperatures and pressures) are varied in quite large limits;
- the volumes of these zones (heat exchangers, condensers, compressor, washing column etc.) are often unknown or are difficulty calculated;
- except the accepted gas phase reactions (2) and (3), some other homogeneous reactions may also take place, mainly at the high pressures.

These are the reasons to develop an adaptive algorithm for modeling of NO conversion in the different zones of the technological scheme:

1) On the base of this developed algorithm is an approximation equation for the degree of NO conversion \( b \) as a function of the factors from equation (7) [5]:

\[ \frac{\beta}{1 - \beta} = \frac{M \gamma_{in}}{1 + 0,34M} \]  \hspace{1cm} (8)

where:

\[ M = k(T_m) \sigma_{in} P_{in}^2 \tau_{av} \]  \hspace{1cm} (9)

\[ \sigma_{in} = 0,5 \sum_{j=1}^{\infty} G_{j}^{in} \]  \hspace{1cm} (10)

\[ \gamma_{in} = \frac{G_{O_2}^{in}}{0,5 G_{NO}^{in}} \]  \hspace{1cm} (11)

2) Using project nitrous gas compositions at the entrances of the different homogeneous reaction zones, the parameter \( M \) from equation (8) is calculated as:

\[ M = \frac{\beta}{(1 - \beta) \gamma_{in} - 0,34 \beta} \]  \hspace{1cm} (12)

3) The average residence time \( \tau_{av} \) is calculated from equation (9) as:

\[ \tau_{av} = \frac{M}{k(T_m) \sigma_{in} P_{in}^2} \]  \hspace{1cm} (13)
The rate constant \(k\) is calculated from equation (6) using the inlet temperature \(T_{in}\).

4) The volumetric flow rate of the gas stream may be calculated as a function of inlet molar flow rate of nitrous gas, inlet temperature and pressure:

\[
v_{in} = 22.4 \sum_{j=1}^{s} G_{in}^{j} \frac{T_{in} + 273.16}{273.16 P_{in}} (14)
\]

5) Finally, the volume of every homogeneous reaction zone \(V_{z}\) may be calculated as:

\[
V_{z} = v_{in} \tau_{av} \quad (15)
\]

According to this adaptive procedure for calculation of the volume \(V_{z}\) of gas phase reaction zone, the NO conversion can be calculated only by input conditions.

**B. Calculation of nitrous gas composition in the exit of the gas phase reaction zone**

The developed method involved the following steps:

1) The initial conditions for this algorithm are:
   a) the adaptive parameters \(V_{z}\) for every gas reaction zone is already known by using algorithm A;
   b) process variables at the entrance of the zone (temperature, pressure, flow rate and composition of the nitrous gas) are also available from the modelling of the unit before the calculated reaction zone.

2) For the investigated zone, the following calculations are possible:
   a) the average residence time \(\tau_{av}\): \(\tau_{av} = \frac{V_{z}}{v_{in}} \frac{3600}{\nu_{in}} (16)\)
   b) the rate constant \(k(T_{in})\), according to the equation (6);
   c) the molar parts of the key components \(\mu_{NO}\), \(\mu_{NO_{2}}\), and component ratios \(\sigma\) and \(\gamma\) according to equations (10) and (11);
   d) the parameter \(M\) (see equation (9)).

3) Solving equation (8) the NO conversion degree \(\beta\) for the gas phase zone is calculated as:

\[
\beta = \frac{M \gamma}{(\gamma + 0.34)M + 1} (17)
\]

4) The composition of nitrous gas in the exit of the zone is defined by the following stoichiometric equations:

\[
G_{NO}^{out} = (1 - \beta)G_{NO}^{in} (18)
\]

\[
G_{NO_{2}}^{out} = G_{NO_{2}}^{in} + \beta G_{NO}^{in} (19)
\]

\[
G_{O_{2}}^{out} = G_{O_{2}}^{in} - 0.5 \beta G_{NO}^{in} (20)
\]

\[
G_{N_{2}}^{out} = G_{N_{2}}^{in} ; G_{H_{2}O}^{out} = G_{H_{2}O}^{in} (21)
\]

**C. Algorithm for temperature losses calculations in the tubes between the units of the technological scheme**

As was noted above, the tubes for nitrous gas flow between the units of flow sheet are in fact adiabatic reactors for NO oxidation. The heat losses to the surroundings have to be calculated in advance, in order to predict the temperature at the exit of the tube (entrance temperature for the next unit). For this purpose the following algorithm is proposed:

1) the NO conversion degree \(\beta\) for the tube is calculated by using the above algorithm B;

2) the heat arising from NO oxidation reaction \(\beta\) in the tube volume is calculated by the expression:

\[
Q_{c} = 14750 \beta G_{NO}^{in} (22)
\]

3) The heat capacity of the nitrous gas \(C_{p,mix}\) for the inlet conditions is calculated as a function of the composition and the temperature:

\[
c_{p,mix} = \sum_{j=1}^{s} \mu_{j} c_{p,j}(T) (23)
\]

where: \(j = 1, 2, ..., 5\) are the numbers of the gas components \((j = 1\) for NO; \(j = 2\) for \(NO_{2}\); \(j = 3\) for \(O_{2}\); \(j = 4\) for \(N_{2}\); \(j = 5\) for \(H_{2}O\))

\(\mu_{j}\) – molar part of the j-th component;

\(c_{p,j}\) – heat capacity of the j-th component \((j = 1, 2, ..., 5)\) are calculated as the next functions of the temperature [2]:

\[
c_{p,j} = a_{h,j} + a_{l,j} \left(\frac{T_{in} + 273.16}{T_{in} + 273.16}\right) (24)
\]

where \(a_{l,j}\) are empirical coefficients for the components of the mixture.

4) The adiabatic temperature change \(\Delta T_{ad}\) is calculated from the equation:
\[ \Delta T_{ad} = \frac{Q_r}{c_{p,\text{mix}} \sum_{j=1}^{G_j} G_j} \]  

(25)

5) For the adiabatic conditions and without heat losses, the temperature at the exit of the tube is:

\[ T_{out}^{ad} = T_{in} + \Delta T_{ad} \]  

(26)

6) Finally, the temperature losses in the tube - \[ \Delta T_{loss} \] is a difference between calculated outlet temperature and experimentally measured temperature \[ T_{exp}^{out} \]:

\[ \Delta T_{loss} = T_{out}^{ad} - T_{exp}^{out} \]  

(27)

RESULTS

The developed mathematical models for homogeneous NO oxidation have been implemented in a computerized information system SNAPi [7].

The computer program has been tested by the data collected in a nitric acid plant from a fertilizer production factory in Devnia, Bulgaria.

The pressures and the compositions at the entrance of each unit in the technological scheme are taken from the simulation of the plant performance. The experimental temperatures at the entrances and at the exits \[ T_{in}, T_{out} \] from each unit are given in Table 1.

The main results of model predictions – estimation parameters of the reaction zones \[ V_j \], the degree of NO conversion \( \beta \) and the calculated temperature losses \( \Delta T_{loss} \) in the tubes between the technological units are also given in Table 1.

The value of \( V_j \) and \( \Delta T_{loss} \) are one quantative prove for the capability of the proposed modelling algorithms. The validity of the mathematical modelling of homogeneous NO oxidation in nitric acid production will be proved by comparison of real plant data and results from the software package SYSTEM, which is created now [8].

### Table 1. Main results of the developed models for the data from nitric acid production in “Agropolichim”, Devnia.

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction zone</th>
<th>( T_{in}, K )</th>
<th>( T_{out}, K )</th>
<th>( \beta % )</th>
<th>( V_j, m^3 )</th>
<th>( \Delta T_{loss}, K )</th>
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<tbody>
<tr>
<td>1</td>
<td>Tube to H.21.06</td>
<td>553</td>
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<tr>
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<td>12,33</td>
<td>15,651</td>
<td>-</td>
</tr>
<tr>
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REFERENCES