

THERMAL NITROGEN OXIDES EMISSIONS FROM FUEL COMBUSTION

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The paper presents an original analytical method for establishing the concentration of thermal nitrogen oxides produced during the combustion processes in the furnaces. The method has been validated by aid of the experimental data obtained burning crude sunflower oil as a fuel. There was a good concordance between the experimental and the proposed analytical data.

1. INTRODUCTION

In the case of fuel combustion, besides nitrogen oxides coming from the nitrogen contained in its structure, there is also nitrogen oxides formed due to the nitrogen found in combustion air.

These oxides, formed from the nitrogen contained into the combustion air can be divided in two distinguished categories:

Thermal nitrogen oxides NO_x^t that are formed in the maximum temperature zone, $T > 1700\text{K}$, following the oxidation of molecular nitrogen due to atomic oxygen.

Prompt nitrogen oxides NO_x^p that are formed in a lower temperature region of the flame, but no lower than 1600 K as result of the interaction of hydrocarbon radicals derived from fuel with atmospheric nitrogen molecules.

To be noticed that, according to [4] the fraction of NO_x^p , within the overall amount of nitrogen oxides formed during the combustion, is small (5% –10%).

2. NITROGEN OXIDES EMISSIONS

Dedicated literature [2] presents a diagram used for the determination of thermal nitrogen oxides emissions, where $K_{\text{NO}_2}^t$ results as a function of the flame temperature and air excess coefficients [Fig. 2.1].

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If we take into consideration the amount of heat Q_t generated by the combustion of a unit mass of fuel, then the emissions of thermal nitrogen oxides are given by the following relationship:

$$C_{\text{NO}_2}^t = K_{\text{NO}_2}^t \cdot Q_t \cdot 10^{-6} \frac{\text{kg}_{\text{NO}_2}}{\text{kg}}, \quad (2.1)$$

where: $K_{\text{NO}_2}^t$ in $\frac{\text{kg}_{\text{NO}_2}}{\text{GJ}}$ and Q_t in $\frac{\text{kJ}}{\text{kg}}$.

Taken into consideration the flue gas volume produced by the combustion of a unit mass of fuel, V_g , the relationship (2.1.) for NO_2^t concentration becomes:

$$C_{\text{NO}_2}^t = \frac{K_{\text{NO}_2}^t \cdot Q}{V_g} \left[\frac{\text{mg}_{\text{NO}_2}}{\text{m}_N^3} \right] \quad (2.2)$$

where: V_g = flue gas volume, in $\frac{\text{m}_N^3}{\text{kg}}$;

It is to be noted that $K_{\text{NO}_2}^t$ depends on the flame temperature in accordance

with the ratio $\frac{e^{\frac{64500}{T_{fl}}}}{\sqrt{T_{fl}}}$ as well as on the square root of the ratio between the concentration of O_2 after the stoichiometric burning and initial concentration of O_2 [2]. This last ratio could be writing:

$$\left(\frac{C_{\text{O}_2}}{C_{\text{O}_2i}} \right)^{\frac{1}{2}} = \left(\frac{0.21 \cdot (\lambda - 1) \cdot V_a^0}{0.21 \cdot \lambda \cdot V_a^0} \right) = \left(\frac{\lambda - 1}{\lambda} \right)^{\frac{1}{2}}, \quad (2.3)$$

where: V_a^0 – minimum humid air volume; λ – excess air coefficient.

Using the flame temperature and the excess air influences [2], for $K_{\text{NO}_2}^t$ is proposed the following analytical relationship:

$$K_{\text{NO}_2}^t = k \cdot \frac{e^{\frac{64500}{T_{fl}}}}{\sqrt{T_{fl}}} \cdot \left(\frac{\lambda - 1}{\lambda} \right)^{\frac{1}{2}}. \quad (2.4)$$

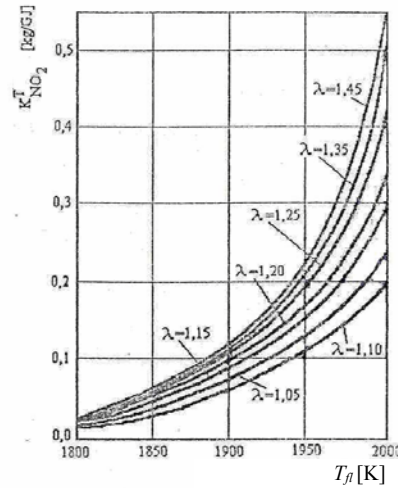


Fig. 2.1 – The influence of flame temperature and excess air coefficient on K'_{NO_2} .

The influence of the flame temperature T_{fl} and of the excess air coefficient on K'_{NO_2} , is illustrated in Fig 2.1 [2]. The analyze of the values obtained for K'_{NO_2} from Fig. 2.1 in connection with the values given by the relationship (2.4) shows that the coefficient k used in (2.4) is not constant and depends on the flame temperature. The values obtained for this coefficient for different temperatures, according to the diagram (2.1) and the relationship (2.4), are noted in the Table 2.1, where $k' = 10^{-14} \cdot k$ and the values obtained for k' and $\frac{1}{k'} \cdot 10^3$ are relative to the flame temperature (Fig. 2.2).

Table 2.1

T_{fl} [K]	1800	1850	1900	1950	2000
k'	69	61	54	49	45
$\frac{1}{k'} \cdot 10^3$	14.49	16.4	18.52	20.4	22.22

A proportional variation of $\frac{1}{k'} \cdot 10^3$ with the flame temperature is shown by the Fig. 2.2, which can be expressed by:

$$\frac{1}{k'} = 38.65 \cdot T_{fl} \cdot 10^{-6} - 0.0551. \quad (2.5)$$

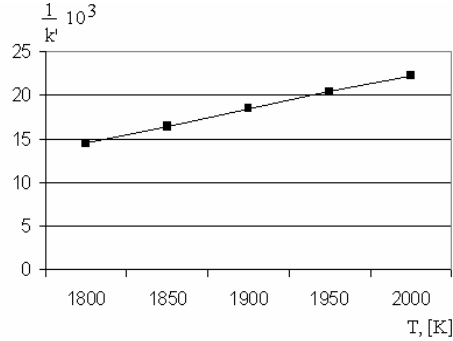


Fig. 2.2 – Dependence of $k' \frac{1}{k'} \cdot 10^3$ on T_{fl} .

Since $k' = 10^{-14} \cdot k$ and taken into consideration the relationship (2.5), for the coefficient k is obtained:

$$k = \frac{10^{14}}{38.65 \cdot 10^{-6} \cdot T_{fl} - 0.0551}. \quad (2.6)$$

The substitution of (2.6) in (2.4) leads to the following relationship for K'_{NO_2} :

$$K'_{NO_2} = \frac{10^{14}}{38.65 \cdot 10^{-6} \cdot T_{fl} - 0.0551} \cdot \frac{e^{-\frac{64500}{T_{fl}}}}{\sqrt{T_{fl}}} \cdot \left(\frac{\lambda - 1}{\lambda} \right)^{\frac{1}{2}} \left[\frac{\text{kg}_{NO_2}}{\text{GJ}} \right]. \quad (2.7)$$

The analytical relationship for thermal nitrogen oxides concentration, NO_2^t , for K'_{NO_2} in mg/GJ and Q_t in kJ/kg, becomes:

$$C'_{NO_2} = \frac{10^{14}}{38.65 \cdot 10^{-6} \cdot T_{fl} - 0.0551} \cdot \frac{e^{-\frac{64500}{T_{fl}}}}{\sqrt{T_{fl}}} \cdot \left(\frac{\lambda - 1}{\lambda} \right)^{\frac{1}{2}} \cdot \frac{1}{V_g} \left[\frac{\text{mg}_{NO_2}}{\text{m}_N^3} \right]. \quad (2.8)$$

The low heat value of the fuel, Q_i in kJ/kg, is:

$$Q_t = Q_i + h_a + h_c, \quad (2.9)$$

where h_a – humid air enthalpy, in kJ/kg; h_c – fuel enthalpy, in kJ/kg.

The flame temperature is considered the maximum value in the burning zone [2] and can be obtained taken into consideration the heat transfer inside the

furnace, to the boiler back, the combustion stage of the fuel and the influence of the flue gas recirculation.

The flame temperature could be calculated with:

$$T_{fl} = \beta_a \cdot T_a (1 - \psi)^{0,25} (1 - r^{1-nr}) \cdot m_c, \quad (2.10)$$

where: β_a – the fuel ratio that was burned in the region between the burner exhaust and the end of the intensive burning with high temperature. For gas and liquid fuels $\beta_a = 0.97 - 0.99$ [2]; T_a – adiabatic burning temperature [K]; ψ – coefficient for thermal efficiency of the boiler back in the flame nucleus region; r – flue gas recirculation degree; n – coefficient for flue gas inlet mode in the furnace; m_c – coefficient for the burner type, $m_c = 1$ for the wall and swirling

burners, $m_c = 0.95 \left(\frac{25}{w_a} \right)^{0.2}$ for coal register burner; w_a is the axial exhaust velocity, in m/s.

Adiabatic combustion temperature can be calculated from the equality of flue gas enthalpy and heat added by burning a unit mass of fuel Q_t , $Q_t = h_g$.

Flue gas enthalpy is:

$$h_g = V_{RO_2} \cdot h_{RO_2} + V_{H_2O} \cdot h_{H_2O} + V_{N_2} \cdot h_{N_2} + V_{as} \cdot h_{as}, \quad (2.11)$$

where: – V_{RO_2} , V_{H_2O} , V_{N_2} , V_{as} – volumes of the flue gas components, in kJ/kg; – h_{RO_2} , h_{H_2O} , h_{N_2} , h_{as} ; – enthalpy of the flue gas components, in kJ/m³ considered at the adiabatic burning temperature, t_a , in °C.

The relationship (2.8), which gives the possibility of an analytical calculation of the thermal nitrogen oxides concentration, produced in the combustion processes in the furnaces, was validated based on the experimental data obtained at the crude sunflower oil burning, presented in [1]. These experiments were made in the Combustion laboratory of the Classical and Nuclear Thermo-mechanical Equipment Chair from University “Politehnica” of Bucharest.

3. CONCENTRATION OF THERMAL NITROGEN OXIDES PRODUCED IN THE COMBUSTION OF CRUDE SUNFLOWER OIL

In order to calculate the concentration of the thermal nitrogen oxides by aid of the analytical relationship (2.8) some preliminary calculations were necessary to establish adiabatic combustion temperature, T_a , flame temperature, T_{fl} , and flue gas volume, V_g .

The combustion calculation was based on the chemical composition of the crude sunflower oils fuel, its low heat value and the excess air coefficient in the flame, during the combustion experiments [1].

3.1. COMBUSTION CALCULATION

The chemical composition of the crude sunflower oil was: $C^i=76.5\%$, $H^i=12.79\%$, $N^i=0.05\%$, $S^i=0.008\%$, $O^i=10.58\%$ and the corresponding low heat value $Q_i^l = 38,142 \text{ kJ/kg}$ [4].

The results of burning calculation consists in: minimum oxygen volume, $V_{O_2}^0 = 2.011 \text{ m}_N^3/\text{kg}$, minimum air volume $V_{a_2}^0 = 9.8619 \text{ m}_N^3/\text{kg}$, carbon dioxide and sulphure dioxide volumes $V_{RO_2} = 1.1429 \text{ m}_N^3/\text{kg}$ and minimum nitrogen volume $V_{N_2}^0 = 7.79 \text{ m}_N^3/\text{kg}$.

The excess air coefficient in the flame during the experiments was. $\lambda = 1.15$.

Based on this value was been calculated the air volume $V_a = 11.34 \text{ m}_N^3/\text{kg}$, the excess air volume $V_{as} = 1.449 \text{ m}_N^3/\text{kg}$, water vapor volume $V_{H_2O} = 1.164 \text{ m}_N^3/\text{kg}$ and dry flu gas volume $V_{gu} = 10.7 \text{ m}_N^3/\text{kg}$.

3.2. ADIABATIC COMBUSTION TEMPERATURE

The experimental crude sunflower oil burning was made in the conditions of the air temperature $t_1 = 18.6 \text{ }^\circ\text{C}$ and oil temperature $t_u = 100 \text{ }^\circ\text{C}$. Based on the oil low heat value Q_i , the heat added burning the unit mass of oil was

$$Q_t = 38,732 \frac{\text{kJ}}{\text{kg}}.$$

After some testes the adiabatic combustion temperature was established to the value $t_a = 1905 \text{ }^\circ\text{C}$, or $T_a = 2178 \text{ K}$ [5]. For this temperature the enthalpies of

the gas components are: $h_{RO_2} = 4,593 \frac{\text{kJ}}{\text{m}_N^3}$, $h_{H_2O} = 3,699 \frac{\text{kJ}}{\text{m}_N^3}$,

$$h_{N_2} = 2,812 \frac{\text{kJ}}{\text{m}_N^3}, h_{as} = 2,906 \frac{\text{kJ}}{\text{m}_N^3}.$$

Introducing the gas component volumes and (2.11) and after calculations the flue gas enthalpy was $h_g = 38,737 \frac{\text{kJ}}{\text{kg}}$. Consequently the relative difference

between Q_i and h_g , at $T_a = 2,178 \text{ K}$, is $\Delta Q = 0.013 \%$.

Heat added to water burning the unit mass fuel can be calculated by aid of the relationship:

$$Q_a = \frac{\dot{m}_a}{\dot{m}_u} (t_2 - t_1) c_a. \quad (3.1)$$

During the experiments the water and oil flow rates were $\dot{m}_a = 590$ kg/h and $\dot{m}_u = 7.12$ kg/h. The water inlet and exhaust temperature were $t_1 = 15.1$ °C and $t_2 = 67$ °C. In this conditions the heat added to water was $Q_a = 17,976 \frac{\text{kJ}}{\text{kg}}$.

The thermal efficiency coefficient ψ , is given by:

$$\psi = \frac{Q_a}{Q_t} = 0.464,$$

for $\beta_a = 99$ and $m_c = 1$, Eq. (2.10) for the flame temperature leads to $T_{fl} = 1845$ K.

Introducing in (2.8) the values for the flame temperature, T_{fl} , and the excess air coefficient, the concentration of the thermal nitrogen oxides is obtained

$$C'_{\text{NO}_2} = 123.8 \frac{\text{mg}_{\text{NO}_2}}{\text{m}_N^3}.$$

3.3. FUEL NITROGEN OXIDES FOR SUNFLOWER OIL

In accordance with [3], the concentration of the fuel nitrogen, for a content of nitrogen in sunflower oil $N_c \in [0 \div 0.5]$ can be estimated with the relationship:

$$C^c_{\text{NO}_x} = \frac{10^{14} \cdot N^i}{3,05 \cdot N^i + 0.982} \cdot \frac{21 - O_2^{st}}{21} \cdot \frac{1}{V_{gu}} \left[\frac{\text{mg}_{\text{NO}_x}}{\text{m}_N^3} \right], \quad (3.3)$$

where: N^i – nitrogen content of the fuel; V_{gu} – dry flue gas volume, $\frac{\text{m}_N^3}{\text{kg}}$.

Taken into consideration the values for N^i and V_{gu} , the value of the nitrogen oxides concentration is $C^c_{\text{NO}_x} = 35.3 \frac{\text{mg}_{\text{NO}_x}}{\text{m}_N^3}$.

According to [4] the NO_x oxides are a mixture of NO and NO_2 in a fraction of 90% NO and 10% NO_2 . This shows that a mol of NO_x has a 31.6 g and consequently the concentration of the fuel nitrogen oxides, NO_x , is:

$$C_{\text{NO}_2}^c = \frac{46}{31.6} \cdot C_{\text{NO}_x}^c = 51.38 \frac{\text{mg}_{\text{NO}_2}}{\text{m}_N^3}.$$

The nitrogen oxides concentration in flue gas is:

$$C_{\text{NO}_2} = C_{\text{NO}_2}^t + C_{\text{NO}_2}^c = 175.18 \frac{\text{mg}_{\text{NO}_2}}{\text{m}_N^3}.$$

3.4. THE CORRECTION OF THE MEASURED NO_x WITH THE FLUE GAS TEMPERATURE

The experimental measures are relative to dry flue gas, the water vapor in the flue gas being condensed in the measure device. The temperature of the dry flue gas can be considered to be about equal with the saturated temperature of the vapor content corresponding to the saturated pressure. For the experimental condition the partial pressure of the water vapor in the flue gas is:

$$p_{\text{H}_2\text{O}} = \frac{V_{\text{H}_2\text{O}}}{V_g} p_0 = 0.13285 \cdot 10^5 \frac{\text{N}}{\text{m}^2}.$$

The corresponding saturated temperature is $t_s = 49$ °C. Taken into consideration the flue gas temperature of $t = 30$ °C the correction of the nitrogen oxides concentration with the temperature is:

$$C_{\text{NO}_2} = C_{\text{NO}_2}^m \frac{273 + t}{273} = 178.69 \frac{\text{mg}_{\text{NO}_2}}{\text{m}_N^3}.$$

The comparison of the analytical and experimental values for nitrogen oxides concentration in the flue gas produced by the combustion of crude vegetable sunflower oil shows a good relative difference of $\Delta C = 1.96\%$.

4. CONCLUSIONS

The analyze of the results obtained for the concentration of nitrogen oxides produced in furnace in the combustion process of vegetable sunflower oil shows a good compatibility between the analytical and the experimental values. The analytical value given by Eq. (2.8) and (3.3) has a relative difference of 1.96% in comparison with the experimental value corrected with the temperature of the dry flue gas.

It is remarkable that the relationship (2.8) proposed for the calculation of the thermal nitrogen oxides concentration, C'_{NO_2} , can be applied for any kind of fuels if the chemical composition, low heat value and excess air coefficient are known.

The relationship proposed for the evaluation of thermal nitrogen oxides emphasizes the temperature influence. The reduction of the flame temperature from 1,845K to 1,830 K leads, according to Eq. (2.8), to a decrease of thermal nitrogen oxides concentration NO_2' with about 20%, from $123 \frac{mg}{m_N^3}$ to $98 \frac{mg}{m_N^3}$.

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