

Prediction of the pollutants generation in natural gas/residual steel gases co-combustion

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Abstract - The effect of co-combustion of residual steel gases (blast furnace and coke oven) and natural gas on the pollutant formation: CO, NO_x, SO₂ was examined in the paper. The residual gases of blast furnace and coke oven are characterized by reduced lower heating values and high content of carbon monoxide and dioxide (CO₂, CO), nitrogen (N₂) and hydrogen sulphide (H₂S). Combustion of these fuels leads to an increased emission of pollutants (CO, SO₂, NO_x). As formation of these pollutants is influenced by O₂ content in flame, the case with less excess air (10% excess air) was numerically simulated on a steam generator furnace. The boiler under investigation is a 230MW, water-tube boiler having two, respectively three vertically aligned burners. The conservation equations of mass, momentum and energy, and equations representing the transport of species concentrations, turbulence, combustion and radiation modelling in addition to CO modelling equations and models describing thermal NO formation, were solved together. The simulation study provided the temperature, NO, CO and SO₂ distribution in the combustion chamber. The simulation results were compared with the actual boiler furnace measurements (corresponding to 25% excess air).

Key-Words - NO formation, SO₂ yield Coke-oven gas and blast-furnace gas combustion, Low temperature corrosion.

I. INTRODUCTION

Coal is the main energy sources in the iron and steel industry. Some of the coal energy is converted to coke oven gas during the production of coke and to blast-furnace gas when the iron ore is reduced with coke to metallic iron. These gases may be recovered and used as fuel in various installations. Their combustion is a direct way to increase the overall efficiency of processes, but this raises a varies problems such as: high emission of NO_x due to the high amount of nitrogen the blast-furnace gas contains, high emission of SO₂ due to the high amount of hydrogen sulphide the coke-oven gas contains and relatively high CO₂ emission (due to the large amounts contain of CO and CO₂), if compared with other hydrocarbon fuels, e.g. natural gas. In certain circumstances in the boiler, particularly when the excess air is large, SO₂ converts into SO₃. The presence of SO₃ in the burning gases leads to the increase of the dew temperature of the gasses and to the risk of reaching this temperature when burning gases cross the terminal surface of heat exchange of the boiler-air preheater, with the initiation of the boiler's low temperature corrosion phenomena.

Besides the demands for GHG reduction due to Kyoto

agreement, Romania, as an EU member, has to respect the national and the EU regulations considering pollutants emissions as well. In Romania, the legislation stipulates for furnace supplied with gas fuel, a maximum emission of 350 mg/Nm³ for NO_x and 35mg/Nm³ for SO₂ for new installations, and a maximum emission of 500 mg/Nm³ for NO_x and 1700 mg/Nm³ for SO₂ for old installations. These concentrations are related to a concentration of oxygen in burning gases of 3%.

To respect these limits we must deal with organizing the combustion or treating the burning gases. The selection of an alternative is determined by cost and the efficiency of the polluting emission reduction.

NO_x formation during the combustion process in gas fired boilers occurs mainly through the oxidation of N₂ from the combustion air and from the fuel by two mechanisms known as thermal NO_x and prompt NO_x. The formation of NO is an extremely complicated problem due to many parameters that influence its formation process. The main parameters are: the flame temperature, the concentration of N₂ and O₂ in flame (determined by the excess air), the concentration of N₂ in fuel, the burner's construction (combustion air swirl angle) and the organization of combustion (staged combustion).

Carbon monoxide is formed during combustion because of either [1]:

- inadequate supply of oxygen, or
- insufficient values of the three T 's, temperature, time or turbulence, e.g.
 - poor mixing of fuel and air;
 - insufficient residence time to complete combustion;
 - quenching of combustion gases.

During combustion of fuels rich in sulphur, or hydrogen sulphide certain amount of produced SO₂ (typically 1–3%) under certain conditions is being transformed into SO₃, which at lower temperatures (below 580°C), reacts with water vapour forming sulphuric acid [10]:



If the temperature of flue gases, containing H₂SO₄ and H₂O vapours, decreases below the dew point, the result is a condensation and the sulphuric acid solution formed has a corrosive action on the heat exchanger metal surfaces, which is the low-temperature corrosion appears.

The numerical calculation of NO, CO is a three-dimensional problem that involves combustion, turbulence and the heat transfer. Computational fluid dynamics (CFD)

models are used to solve the complex three-dimensional models for equipment design and operational changes. The reacting system is modelled by the equilibrium chemistry formulation. This formulation is based on the assumption that chemistry is fast enough to preserve chemical equilibrium at the molecular level. Such assumption is valid for main reactions and species in the combustion process but it fails in the case of slow kinetics like NO_x and SO_3 formation.

While NO_x models give acceptable results in the Fluent code used in this work, the sulphur trioxide production is not very well represented. Problem lies in the finite kinetic character of SO_3 reactions [11].

By all means, among the cheapest solutions to reduce Kn_{ox} emission there is an efficient matching of aerodynamic and combustion parameters and the improvement in designing the burners. These solutions can be capitalized by means of predicting procedures of polluting emissions.

As the excess air in the furnace influences a lot the NO , CO and SO_3 formation the paper presents the results of numerical modelling of the co-combustion of natural gas with blast-furnace gas and coke gas in the furnace of an energetic for the case with reduced excess air than the actual one (10% instead of 15%).

II. BOILER MODEL

The combustion of the two artificial fuels (coke gas and blast-furnace gas) in the furnace of the 230 MW boiler is made simultaneously with the combustion of natural gas. The two artificial fuels have a reduced heating value and to produce the heat flow in the furnace only with them would require very large flows. For this reason natural gas (or fuel oil) is used. The volumetric composition of the fuels can be seen in Table 1.

Due to the fact that the furnace of the boiler is made of two identical chambers the investigation has been made on one of these chambers. The burner consists of four coaxial jets. Starting from the axis of symmetry, it is composed of a natural gas central jet, surrounded by an air flow, followed by a coke or blast-furnace gas flow and air at the periphery.

The burners are displayed on the walls of the furnace in the following way: on the frontal wall, at the upper levels 1 and 2 are placed the natural gas burners, and at the lower level, the burner fuelled with coke-oven gas and natural gas, on the lateral wall are arranged vertically the two burners fuelled with blast-furnace gas and natural gas.

Table 1 Characteristics of gas fuels.

Analysis vol. %	Blast-furnace	Coke-oven	Natural gas
Carbon dioxide, CO_2	17.98	3.03	-
Oxygen, O_2	0.21	0.689	-
Carbon monoxide, CO	21.21	8.498	-

Hydrogen, H_2	6.9	51.158	-
Methane, CH_4	0.3	21.068	99.3
Ethane, C_2H_6	-	1.683	-
Hydrogen sulphide, H_2S	0.3	6.174	-
Nitrogen, N_2	53.1	7.7	0.7
Lower heating value, kJ/Nm^3	3431	17166	35523

In Fig. 1 can be seen the way the burners are displayed on the furnace walls. The air jet is swirled (it goes tangentially into the air box). The burners are designed to operate combined with natural gas/oil and coke-oven gas or blast-furnace gas. The modelling of flow, combustion and pollutant formation has been done beginning with the exit of the jets from the burner (air and fuels), from their interaction area.

The Table 2 lists the operation conditions of the investigated furnace boiler.

This investigation has been made to visualize the flame of each burner and the flames interaction for the whole furnace to emphasize the correlation between the parameters of thermogasdynamics and the pollutant formation.

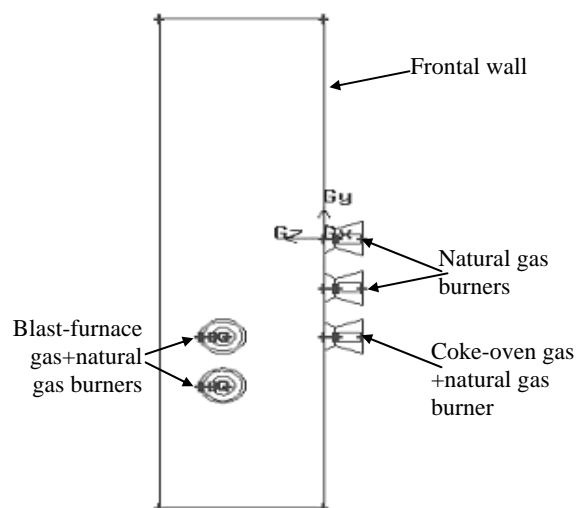


Fig.1. Burners display on the walls of the furnace.

Table 2. Operating conditions.

<i>Natural gas operating conditions</i>	
Natural gas flow rate, Nm^3/h	658
Air flow rate, Nm^3/h	6645.8
Air temperature, $^{\circ}\text{C}$	260
Excess air, %	10

<i>Coke-oven & blast-furnace operating conditions</i>	
Coke-oven gas flow rate, Nm^3/h	10000
Blast-furnace gas flow rate, Nm^3/h	3500
Air flow rate, Nm^3/h	7283/16404
Air temperature, $^{\circ}\text{C}$	260
Excess air, %	10

Furnace operating conditions

Number of natural gas burners	2
Number of coke-oven burners	1
Number of blast-furnace gas burners	2
Static pressure, atm	1
Temperature of walls, °C	380

III. MATHEMATICAL MODEL

The conservation equations for mass, momentum and energy, and transport equations were solved to provide predictions of the flow pattern, thermal and pollution characteristics of reacting flows inside the considered boiler furnace. The operating parameters include the excess air, combustion air temperature and air jet swirl angle.

The equations for conservation of mass, momentum and energy and the equations for species transport may be expressed in the following general form [3]:

$$\partial(\bar{\rho} \bar{u}_j \Phi + \bar{\rho} \overline{u_j \phi}) / \partial x_j = \partial(\Gamma_\phi \partial \phi / \partial x_j) / \partial x_j + \bar{\rho} S_\phi \quad (2)$$

where Φ is the dependent variable and u_j is the velocity component along the coordinate direction x_j ; $\bar{\rho}$ is the fluid density; Γ_ϕ is the diffusion coefficient and S_ϕ is the source term.

Eq. (2) stands for the mass conservation equation when $\Phi=1$; the momentum conservation equation when Φ is a velocity component; the energy equation when Φ is the stagnation enthalpy; or the transport equation of a scalar when Φ is a scalar variable such as mixture fraction. The present work utilized the k- ϵ turbulence model. The equations for Reynolds stresses and turbulent scalar fluxes are [3]:

$$-\overline{\rho u_i u_j} = \mu_t (\partial \bar{u}_i / \partial x_j + \partial \bar{u}_j / \partial x_i) - 2 \rho k \delta_{ij} / 3 \quad (3)$$

$$-\overline{\rho u_j \phi} = \Gamma_\phi \partial \phi / \partial x_j \quad (4)$$

where $\Gamma_\phi = \mu_t / \mu_t$ and μ_t is the turbulent viscosity:

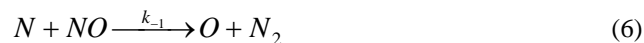
$$\mu_t = c_\mu \rho f_\mu K^2 / \epsilon$$

c_μ , f_μ and σ_ϕ are constants.

The nitrogen oxides can be formed or destroyed during the combustion process by two separate reaction processes, which are classified as thermal NO and prompt NO.

Thermal NO is formed by oxidation of atmospheric and fuel molecular nitrogen at relatively high temperatures in fuel-lean environments, and has a strong temperature-dependence. The prompt NO is formed by combination of molecular nitrogen in the air and fuel with fuel in fuel-rich conditions. Many investigations have shown that the prompt NO contribution to total NO from stationary combustors is small [3].

The thermal NO process is described by the Zeldovich mechanism [5]:



The parameters for the thermal NO reactions are given below:

$$k_1 = 1.8 \cdot 10^8 \exp(-38370/T), \text{ m}^3/(\text{mol}\cdot\text{s}) \quad (9)$$

$$k_{-1} = 3.8 \cdot 10^7 \exp(-425/T), \text{ m}^3/(\text{mol}\cdot\text{s}) \quad (10)$$

$$k_2 = 1.8 \cdot 10^4 T \exp(-4680/T), \text{ m}^3/(\text{mol}\cdot\text{s}) \quad (11)$$

$$k_{-2} = 3.8 \cdot 10^3 T \exp(-20820/T), \text{ m}^3/(\text{mol}\cdot\text{s}) \quad (12)$$

The equation for NO species transport is [3]:

$$\partial(\rho U_j Y_{NO}) / \partial x_j = \partial(\Gamma_{NO} \partial Y_{NO} / \partial x_j) / \partial x_j + S_{NO} \quad (13)$$

where Y_{NO} is the mass fraction of NO in the gas phase and S_{NO} is the NO source term due to thermal NO mechanisms:

$$S_{NO} = M_{NO} d[NO] / dt \quad (14)$$

$$\frac{d[NO]}{dt} = \frac{2[O](k_1 k_2 [O_2][N_2] - k_{-1} k_{-2} [NO]^2)}{k_2 [O_2] + k_{-1} [NO]} \quad (15)$$

$$[O] = 36.64 T^{0.5} [O_2]^{-0.5} \exp(-27123/T) \quad (16)$$

where all the concentrations are expressed as mol/m³.

The CO oxidation reaction



is a fast and somewhat reversible reaction at high flame temperature. The reaction scheme, as developed by Howard, can be represented as [1]:



$$d[CO]/dt = 1.3 \cdot 10^{14} [CO][O_2]^{0.5} [H_2O]^{0.5} \exp(-151000/T),$$

$$\text{mol}/(\text{cm}^3 \cdot \text{s}) \tag{22}$$

for a wide range in temperature (570-2000°C).

IV. RESULTS AND DISCUSSIONS

The operational mode with reduced excess air (10% instead of actual 15%) was investigated. The results are given for the furnace exit. The temperature distribution and the concentrations distribution of O₂, CO and SO₂ are shown in the vertical sections which go through the axes of the burners. The heat that is released by gases combustion is emphasized by the distribution of temperatures which can be seen in Fig. 2. The maximum of temperature (2000°C) is situated in the area where the jets of the coke-oven gas and blast-furnace gas burners interact. Near each burner's air inlets, temperature is lower (about 850°C) due to the fact that combustion is poor in fuel. This non-uniformity of the thermal field disappears at the furnace exit. The predicted temperature at furnace exit (1330°C) is a little higher than that measured temperature for 15% excess air (1295°C).

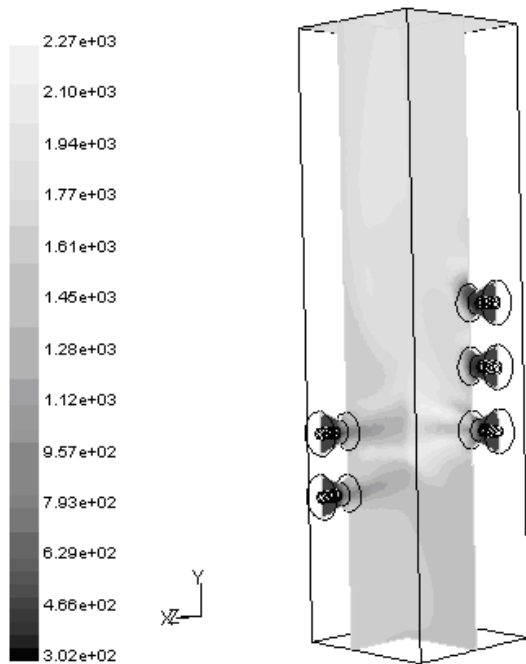


Fig. 2. Gas temperature distribution (K).

The predicted concentrations of CO are high in the areas where the flame is reach in fuel, and the jets of the blast-furnace gas and the coke-oven gas burners (Fig. 3). The maximum concentration of CO is $1.96 \cdot 10^{-1}$ % (mass) and it gradually decreases towards $0.164 \cdot 10^{-1}$ % (mass) as CO mixes and reacts with O₂ in the upper area of the furnace. The high concentrations of CO influence both the temperature of the mixture and the concentrations of O₂ and CO₂. It was expected an increase in CO concentration due to the reduced excess air.

Even with less excess air the CO concentration is low, almost equal to that corresponding to 15% excess air.

The predicted concentrations of O₂ can be seen in Fig. 4. From a value of 23 % (mass) at the outlet of each burner, the O₂ concentration reaches a value of 2.35% after combustion is completed. At the exit of the furnace, the O₂ concentration is 0.015% (mass), which means that there is an adequate amount of excess air in the furnace.

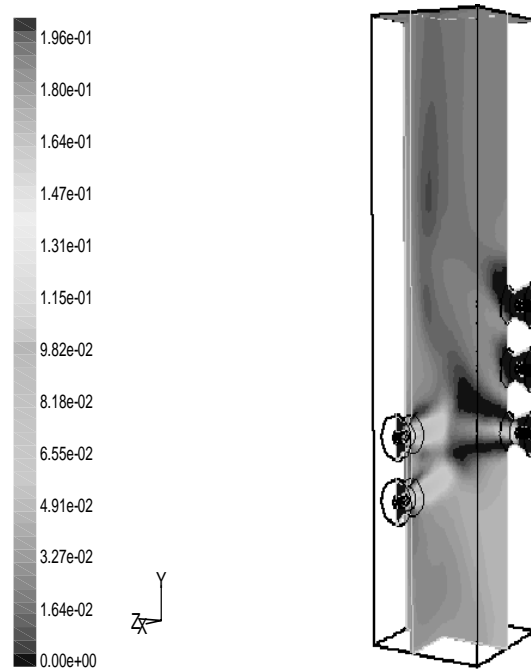


Fig. 3. Carbon monoxide concentration (% mass).

The presence of oxygen in the post-combustion area is undesirable because it leads to the increase of the conversion rate of SO₂ into SO₃ and eventually to the occurrence of the boiler's low temperature corrosion phenomenon. With less excess air in furnace it is expected a lower conversion rate.

We can see in Fig. 5 that only the coke-oven gas burner have an average content of SO₂ of 2300mg/Nm³, which means that its value is higher than the one stipulated by law.

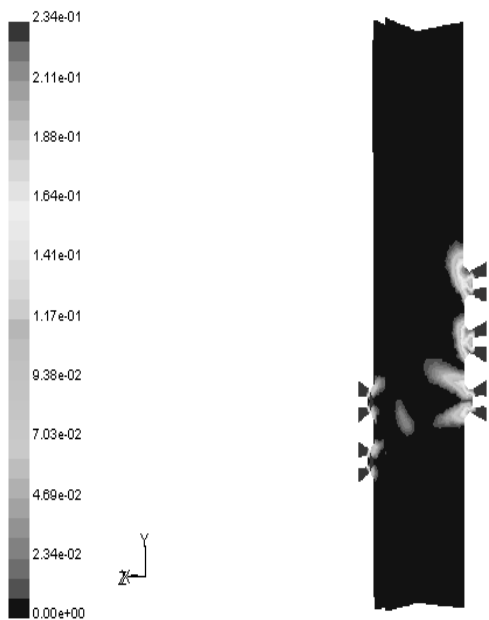


Fig. 4. Oxygen concentration (% mass).

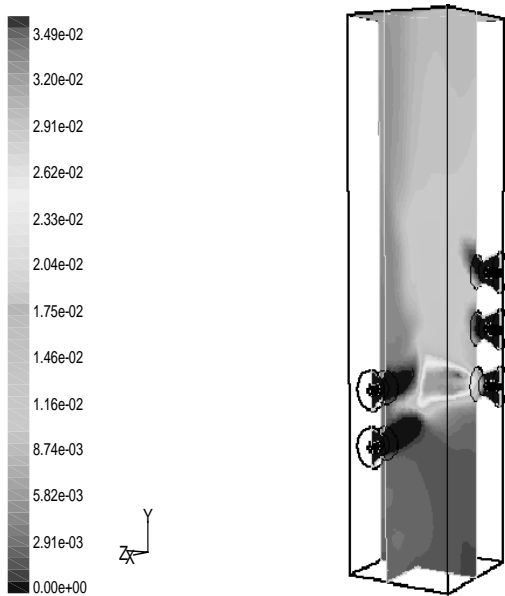


Fig. 5. SO₂ concentration (% mass).

The predicted NO concentrations can be seen in Fig. 6. The NO formation occurs during the burning process and the main mechanism of formation is the thermal one. That is emphasized by the high concentrations of NO in the zones with high temperatures of the flame (260-330 ppm) and low concentrations of NO in the zones with low temperature (50-120 ppm). Mixing within the furnace results in an average NO value of 270 ppm (554 mg/Nm³) at the furnace exit, corresponding to an O₂ concentration of 1.5 % (vol.). If we recalculate the NO emission for a concentration of O₂ of 3%, we obtain a value of 608 mg/Nm³. This value of the predicted

NO concentration is higher than the value stipulated by law, but is lower than that corresponding to 15% excess air (753 mg/Nm³).

V. CONCLUSIONS

Three dimensional simulation of the natural gas/residual steel gases (blast furnace and coke oven) co-combustion in the furnace of a 230MW steam boiler was presented in this study. The simulation provided insight on the correlation between the maximum furnace temperature and excess air on the CO, SO₂ and NO_x concentration. The results have shown that the decrease in excess air results in an increased exit temperature, almost the same CO and SO₂ concentrations and reduced NO concentrations. As the SO₂ to SO₃ conversion rate depends on O₂ concentration it is expected a decrease of SO₃ concentration and therefore an alleviation of low-temperature corrosion of the steam boiler surfaces (air preheater, flue gas channels) is expected. Although the reduction of air excess leads to a reduction of pollutant concentrations, the pollutant emissions are higher than the maximum values that have been accepted and other techniques as flue gas recirculation, change in aerodynamic conditions in the furnace and burners configuration should be considered.

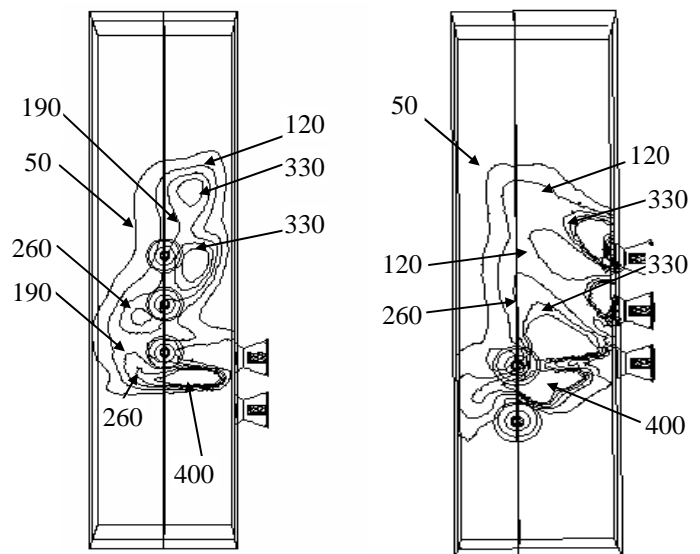


Fig. 6. Concentration of NO_x (ppm).

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