Ovidius University Annals of Chemistry Volume 20, Number 1, pp.137-141, 2009

The prediction of flue gas emissions from the combustion in the industrial tubular heaters

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Abstract. The monitoring of gaseous emissions in a refinery is complex and difficult task requiring special equipment and operators in good physical shape. Some of these emissions could be calculated from other measured data from fixed analysis points. This shall decrease the number of determinations in hazardous circumstances. The authors of this study worked out some equations for the correlation of the main combustion emissions (CO_2, NO_x) with the oxygen content of flue gas and the temperature at the stack. Even though the CO_2 emissions could be predicted by stoechiometric calculations, a model based on statistical processing of hundreds of data is easier to apply; this is why, the authors searched for simple and exact equations. The prediction of CO_2 and NO_x was made versus the the oxygen content of flue gas and the temperature at the stack, which can be measured with fixed sensors. Finally, the prediction of flue gas emissions can be performed by replacing the costly and dangerous sampling, using accurate mathematical model.

Keywords: NO_x emissions, modeling, flue gas monitoring

1. Introduction

The main pollutants in the air proceeding from industrial activities are: CO_2, CO, NO_x, SO_x and particulates. Following the Directive 2000 in Europe and the Environmental Protection Act 1990 in USA, the monitoring of these emissions and their balance are compulsory for any industrial actor. The prediction of the emissions is desirable for industry since the monitoring process requires a large number of analytical determinations in hazardous circumstances and expensive equipment. The modeling of different emissions was more interesting for the cement industry and for coal combustors by now [1-4], but it could be done for the oil processing industry too, taking into account the large amount of emissions in this sector.

The most important source of CO_2, CO, SO_2 and NO_x emissions in an oil refinery is the combustion in the industrial heaters. Since the emissions of sulfur oxides and CO_2 depend only on the combustible's composition, the emissions of CO depend on the excess air for combustion and those of NOx on a few factors: the temperature of the burning process, the air excess, the geometry of the burners [5].

Taking into account these facts, the present study was designed to find correlations for the prediction of some pollutants, thus reducing the equipment and the number of determinations.

2. Experimental

The experiment took place in a refinery were data from the monitoring program were acquired. The study was limited to vertical tubular parallelepiped heaters. Data from other type of heaters (boilers, heat economizers, Claus ovens) were far from the precedent because of very different combustion parameters and geometry.

The monitoring program consists on sampling the flue gases from each combustor and determinate the concentration of CO_2, CO, NO_x, SO_2 and the temperature at the stack. Also, determination of these pollutants in six points around the refinery is done, in order to quantify the imissions. The

ISSN-1223-7221

frequency of these determinations is set at twice a month, and a portable analyzer is used.

The gas analyzer MSI Compact 2500 is a portable apparatus for multiple measurements the in the analysis of flue gas emissions. It is endowed with a standard proof stick for sampling. The sample point is located at two third from the baseline of the heater's stack. The list of parameters, measurement principle and precision are presented in Table 1.

The measurements are instantaneous but they can be correlated among them and also with the fuel composition. By consequence, the CO_2 is calculated from the fuel composition alone, since the air excess is calculated from the fuel composition and oxygen in flue gas, in stoechiometric calculations.

The data during a year long were acquired and 162 sets of complete data were available.

The average minimum and maximum of the measured values are presented in Table 2. The NO_x values correspond to the actual concentrations of O_2. In order to be compared they have to be "normalized" at 15% vol O_2 [5].

Table 1. The main characteristics of the gas analyzer MSI Compact 2500

List of parameters	**Measurement principle**	**Measurement range**	**Precision**
Air temperature	PTC resistor	0-100°C	1°C
Gas temperature	NiCr-Ni thermocouple	0-1200°C	1°C
Oxigen,O2	Electrochemical sensor	0-20,9% vol.	0.1%
Carbon monoxide,CO	Electrochemical sensor	0-4000 ppm vol.	1 ppm
Carbon dioxide,CO2	Calculated	From the fuel composition	0.1%
Nitrogen oxides ,NOx	Electrochemical sensor	0-4000 ppm vol.	1 ppm
SO_2	Electrochemical sensor	0-4000 ppm vol	1 ppm
Air excess	Calculated	1-99	0.01

Table 2. The experimental data

Parameter	U.M.	Average	Minimum value	Maximum value
Oxygen in flue gas	% vol	7.8	1.5	15.0
CO_2 in flue gas	% vol	7.3	4.8	8.6
NO_x in flue gas	ppm vol	236	83	398
Temperature at the stack	K	629	374	910
Fuel gas composition:	%vol			
C_1		42.27	7.87	60.04
C_2		20.26	1.72	25.19
C_3		8.02	1.95	17.11
C_4		4.65	1.04	11.99
C_5^+		3.37	0.3	10.38
H_2		15.19	5.74	30.08
CO, CO_2, O_2, N_2		6.24	0.56	41.16
Calorific power of flue gas at 15°C/15°C	Kcal/m^3	11133	6072	14457

The formula for this conversion is the Eq.(1):

$$NO_{x\_15\%} = (NO_x - NO_{xa})\left(\frac{5.9}{20.9 - O_2}\right)\cdot n \qquad (1)$$

where: NO_x –measured during test;

NO_{xa}- the ambient concentration of nitrogen oxides;

n- the ambient correction factor

The Eq.(1) can be simplified by considering the ambient concentration of NO_x as negligible, and the factor n equal to 1 for this application.

The data were processed in Matlab and Excel using plotting and curve fitting facilities.

3. Results and discussion

Some observations were made concerning the correlation between the air coefficient at combustion α and the O_2 content in flue gas on the one hand and between α and the CO_2 content in flue gas on the other hand. In the first case, the O_2 content increases with α following a logarithmic function, in the second case the CO_2 decreases with α, following a power function, because of diluting the CO_2 in flue gas with α increasing. The graphical correlations are given in Fig. 1 and Fig. 2.

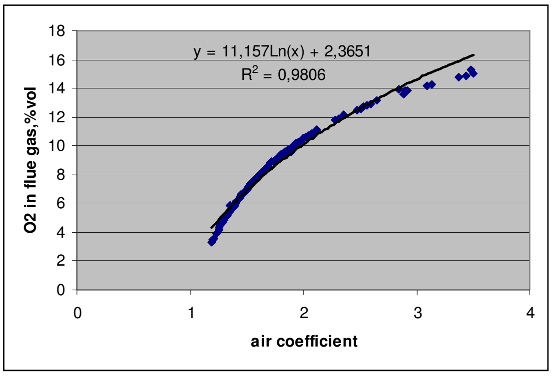

Fig 1. The variation of O_2 content in flue gas with the air coefficient α

By processing the data, the equations (2) and (3) resulted:

$$y = 11.157\ln x + 2.3651 \qquad (2)$$
$$r^2 = 0.9806$$

$$y = 11.768x^{-0.9831} \qquad (3)$$
$$r^2 = 0.9656$$

The Eq.(2)describes the O_2 content vs. the air coefficient α correlation and the Eq.(3)describes the variation of CO_2 content with the air coefficient α.

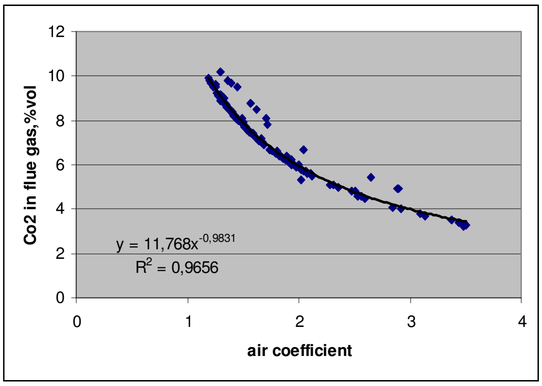

Fig 2. The variation of CO_2 content in flue gas with the air coefficient α

These correlations are interesting but only the first is important because it allows the calculation of the air coefficient and of the excess air for combustion only by using the data acquired with the O_2 sensor, without knowing the fuel composition. The second correlation is useful but indirectly since first the air coefficient would be calculated with the Eq.(2). This is why, the direct correlation of the CO_2 content with the concentration of the O_2 in flue gas (which can be measured with a fixed sensor for oxygen) is considered to be more useful. The correlation is presented in Fig. 3 and the Eq.(4) describes it.

$$y = -0.5516x + 11.769 \qquad (4)$$
$$r^2 = 0.962$$

The Eq.(4) is as good as the Eq.(3) speaking on the correlation coefficient r^2.

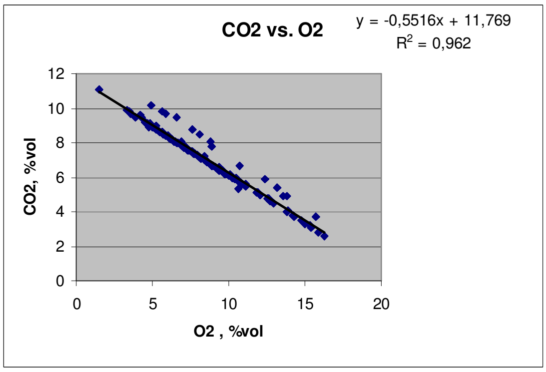

Fig. 3. The variation of CO_2 content in flue gas with O_2 concentration

Trying to correlate the NO_x concentration in flue gas with other measured parameters, we observed that NO_x content increases with the temperature at stack and with the excess air so that a 3 D plot was done as seen in the Fig. 4.

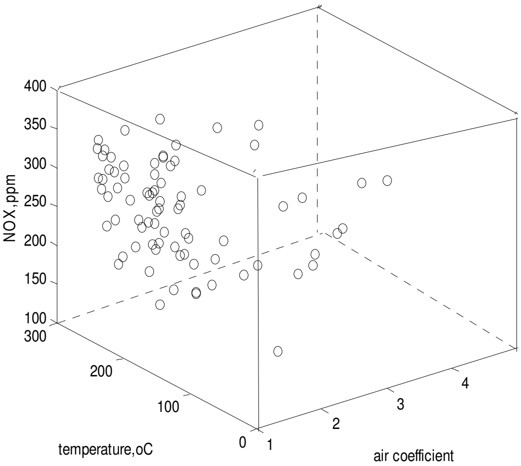

Fig.4. 3D-plot of air coefficient α- temperature at the stack -NO_x in flue gas

From Fig. 4, one can see that experimental points can barely be correlated and this is due to the fact that NO_x concentrations are measured in different conditions. It was necessary to "normalize" the concentrations by expressing them in the same conditions, as recommended in literature [5], at 15% vol O_2, with the Eq.(1). Then, separate correlations were tried: $NO_{x\_15\%}$ vs.O_2 in flue gas and $NO_{x\_15\%}$ vs. temperature at stack [K].

As seen in Fig. 5 and Fig. 6, these correlations have poor coefficients (r^2= 0.70 and r^2=0.40 respectively), mainly because of the fluctuations of the NO_x measured with the portable equipment.

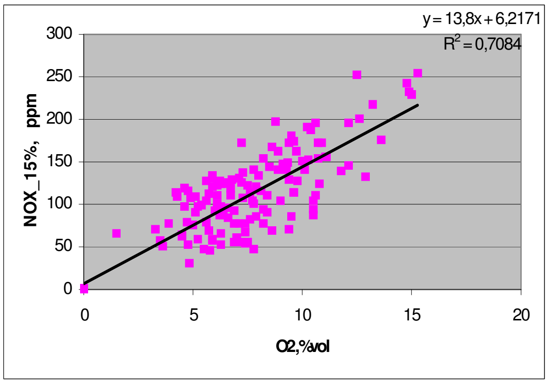

Fig.5. The variation of $NO_{x\_15\%}$ with O_2 in flue gas

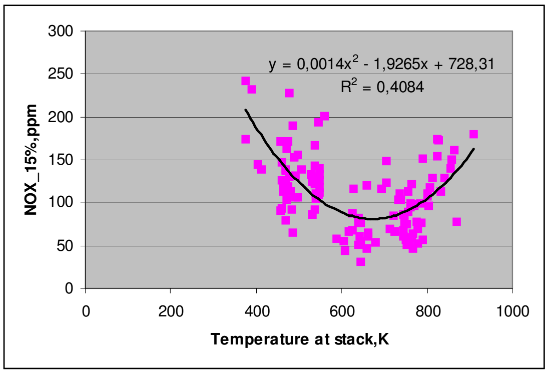

Fig.6 The variation of $NO_{x\_15\%}$ with temperature at stack

The flow of flue gas at the stack is inconstant and NO_x values can vary by dozens in a second. However, one can combine these separate equations, in order to obtain an improved model, the Eq.(5):

$$NO_{x\_15\%} = [(13.8x + 6.2)(0.0014y^2 - 1.92y + \\ +728)]^{0.5} \qquad (5)$$

In the Eq. (5) x represents the concentration of O_2 in flue gas (%vol) and y represents the temperature at the stack (K). This equation allows the prediction of the $NO_{x\_15\%}$ concentration (ppm vol) through two directly measurable parameters.

This model proved to be reliable since the $NO_{x\_15\%}$ calculated with the Eq.(5) differs from the measured $NO_{x\_15\%}$ by 4.2% (average) and a medium standard deviation of 26 ppm is good. These errors are acceptable taking into account that the experimental data were affected by measurement errors due to the specific of data acquiring system.

4. Conclusions

The equations for the prediction of NO_x and CO_2 emissions worked out in this study are simple and accurate enough for the industrial use. The model is valid only for vertical tubular parallelepiped heaters, since for other geometries, the model for NO_x is strongly affected. It was checked on 8 industrial tubular heaters, of various capacity and size. The measured data were acquired twice a month, during a year long. The furnaces ran with fuel gas containing: C_1 (methane): 7.87-60.04% vol, C_2: 1.72-25.19% vol, C_3:1.95-17.11%vol, C_4: 1.04-11.99%vol, C_5^+: 0.3-10.38%vol, H_2: 5.74-30.08%vol. The O_2 concentration in flue gas varied between: 1.5-15.0%vol, the temperature at the stack was: 374-910 K, and the measured values for CO_2 were 4.8-8.6% and NOx concentration varied between 83-398 ppm at the stack conditions.

The prediction of CO_2 concentration is based only on the measured O_2 concentration in flue gas and not on the combustible composition, as at present.

Also, the prediction of NO_x is based on the same measured O_2 concentration in flue gas plus the temperature at the stack. This is an important achievement since the expensive equipment for the measurement is avoided.

The CO concentration wasn't interesting for this study since the air coefficient was over 1.3 and the temperature at the stack was moderate most of time, so the concentration of CO is usually zero, rarely reaching a few ppm. One could give up the monitoring of CO at the stack of tubular vertical heater.

So, instead of measuring the emissions at altitude with portable equipment twice a month, the stack of the heater should be equipped with fixed sensors for oxygen and temperature, and the CO_2 and NO_x emissions could be predicted with the equations worked out in this paper. The monitoring would be more effective since it would be continuous and unaffected by momentum measurements, as now. Also, the SO_2 emissions can be found easy by stoechiometric calculations.

5. References

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