Prediction and Minimisation of NOx Emissions from Industrial Furnaces Using PCA

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Abstract: This paper investigates the possibility of using PCA to produce an empirically based model for predicting the emission rate of Oxides of Nitrogen (NOx) from oil refinery furnaces. The purpose of the model is to enable better management of the furnaces, and reduce potentially harmful emissions. Principal Component Analysis (PCA) was used to build a series of models to predict NOx emissions from a number of furnaces. The models produced were proven to be robust, with relatively high accuracy, and are able to predict NOx levels over the range of values sampled. The models can be integrated with the refinery operating system to predict NOx emission rates on a continuous basis.

1. INTRODUCTION

Oxides of nitrogen, (NOx) mainly consist of nitric oxide (NO) and nitrogen dioxide (NO_2) and are produced in combustion processes. Many texts, including Cheremisinoff [1993], list the potential hazards of NOx emissions. It is primarily for this reason that regulatory bodies place restrictions on the emission of such pollutants, prompting companies relying on combustion processes to monitor pollutant emissions and thus take action when such limits are exceeded [Wight, 1994].

We must first understand the processes occurring before we can accurately model combustion. Hesketh [1991] gives a general stoichiometric combustion equation for hydrocarbon based fuels, in the form.

$$C_mH_n + (m + n/4)\, O_2 \rightarrow mCO_2 + (n/2)H_2O \qquad (1)$$

where: m and n are the number of atoms of carbon and hydrogen (respectively) being combusted. The stoichiometric equation (1) is correct for "complete" combustion where all reactants are consumed totally and react fully. However complete combustion is rarely the case in practice. Other products produced by combustion, can include: carbon monoxide (CO), carbon dioxide (CO_2), oxides of sulphur, oxides of nitrogen, smoke, fly ash, metals, metal oxides, metal salts, aldehydes, ketones, acids, polynuclear hydro-carbons, and many others [Cheremisinoff, 1993].

These by-products may be generated either from impurities in the fuel or from components of the combustion air. However, the formation of these products (and respective stack emission rates) can be greatly decreased by optimal management of the combustion process [John Zink Company, 1984].

For NOx to be formed during combustion processes, nitrogen in some form must be present in the reactants. NOx formed from nitrogen in the fuel is termed Fuel NOx, while that formed from atmospheric nitrogen is termed Thermal NOx [John Zink Company, 1984]. In most situations the Thermal NOx mechanism provides the greatest contribution to the overall NOx concentration [John Zink Company, 1984]. At an Australian Oil Refinery (AOR – name withheld for reasons of confidentiality) since the furnace fuel contains negligible (<1 molar % conc.) nitrogen, hence Thermal NOx is the main mechanism for NOx formation.

It is possible to gain a large reduction in NOx levels by manipulating (residence) time, temperature and oxygen content of flames [De Nevers, 1995]. Similarly, the important process parameters for NOx emission are: fuel composition, combustion air temperature, excess air and furnace temperature. Fuel composition is "the single most important factor affecting NOx formation" [John Zink Company, 1984].

As with most refineries, AOR utilises furnaces extensively to provide heat and steam for process requirements. Two furnaces are discussed in this paper: F1 - a series of 3 boiler units (labelled as F1a, F1b, & F1c), and F2 - a single heater unit. The furnaces are typical of moderate to large industrial box heaters or boilers, with the only notable exception that F1 serves the task of oxidising carbon monoxide (CO) from another refinery unit. The CO is added with the air entering the combustion chamber, and sufficient excess air is provided to perform oxidation. A major contributing factor to AOR NOx emissions is the high hydrogen content (~90%) of the fuel gas. Hydrogen burns with a high peak flame temperature thus increasing Thermal NOx levels.

The refinery is also subject to government regulatory control and the stack emissions (including NOx) are subject to licence limits. Due to strict operating parameters and process requirements at industrial facilities such as AOR, there exists limited scope for operational changes without producing detrimental effects on the product. For this reason, it was chosen to concentrate on two parameters (which had the largest scope for variation and are important to NOx generation). The two important parameters were excess air and furnace temperature, and these were intentionally varied during sampling. However other parameters are included in the model.

There are numerous experts in the field of combustion and combustion modelling. Lixing [1993] has spent many years studying and modelling combustion processes. Xu et al. [1998] are also leaders in the emissions field of combustion modelling and NOx modelling. Their approach is to model the flow fields, chemical reactions and energy flows using partial differential equations. The governing equations are complex and use many parameters to attempt to describe the very complicated flow fields and chemical reactions. Considerable computational power and time is needed to obtain solutions to sufficient accuracy. Such models, while very useful during furnace/burner design and construction, are not easily used by industry. Therefore a more simplified modelling approach is required.

The reason for this study was twofold. The AOR refinery wished to know if it was possible to reduce NOx emissions from some of their furnaces, by making simple process/operational changes rather than installing add-on equipment, and secondly they wished to have a method of continually tracking or predicting emissions, even

with varying process conditions. Empirical modelling is best able to take into account any unusual design/technological features which may influence NOx levels. An empirical model using process telemetry data as the input variables is the most useful type of model for the process operators to use, as the input data can be obtained easily. Thus NOx emissions can be continually minimised and so it can be ensured that licence limits are not exceeded.

2.   METHODOLOGY

An Enerac 3000 combustion analyser (manufactured by Energy Efficiency Systems, Inc.) was selected to take NOx samples. The Enerac conforms to US EPA provisional reference method EMTIC CTM-022.WPF for portable NOx analysers [Lear Seigler, 1995].

Other equipment was used to measure necessary parameters: an S-Type pitot-tube to measure velocity of the exhaust gas in the stack and a thermocouple/electronic thermometer to measure temperature. All measurement equipment and measurement procedures conformed to US EPA reference methods [Wight, 1994].

A total of 15 samples were taken from F1 and 52 from F2. Sampling consisted of: installing the equipment in the stack and taking initial measurements of the NOx emission rate. Following this, one process variable was varied while the other variables were fixed to as great an extent as was possible (some of the variables are related (e.g. fuel flow and furnace temperature)). The parameter being varied was gradually increased or decreased (with samples being taken at periodic intervals 10 mins. - 2hrs, after the process had been allowed to stabilise. This was repeated for other variables. Following sampling, data was collected from refinery telemetry units, to obtain process operating conditions for the exact times that sampling was conducted. The main variables are process temperatures (stack temperature/firebox (furnace) temperature/product temperature), fuel consumption rates (tonnes per day), steam generation rates (for boilers), oxygen concentrations, and (for F1) the amount of flue gas (stack gas) which is being recycled (regenerated) to oxidise CO generated by another process. This data was then collated with the sampling data for modelling.

When conducting sampling at F1, it was the intention to hold two of the boilers (F1b and F1c) constant whilst the third (F1a) was varied. Some variation was noted in the parameters of F1b and

F1c. However the modelling process is able to cope with such variation. All three units were operating at identical conditions when sampling commenced.

The sampling data set for each furnace was randomly separated into two approximately equal subsets. One subset was used for model calibration/construction, while the second was used for validation of the model.

A mathematical/statistical package known as SIRIUS (developed by Pattern Recognition Systems) was used to conduct the modelling. SIRIUS offers a range of features for modelling, including both Principle Component Analysis (PCA) and Partial Least Squares (PLS) [Kramer, 1998 and Massart et al., 1988]. PCA was used, as it is best able to cope with factors such as co-linearity of variables and variable interaction, both of which are likely to occur when modelling complex chemical systems. Various methods of data weighting and standardising are offered by the program, and most of these were used during preliminary modelling in an attempt to determine the best method. The suitability of each method was determined by the 'goodness of fit' of the resultant model, goodness of fit being determined by various parameters generated by SIRIUS, including R^2, Standard Error of Validation (SEV), and Standard Error of Prediction (SEP). Kramer [1998] and Massart et al [1988] give a detailed explanation of the calculation of SEV and SEP as performed by SIRIUS. According to Kramer [1998], the equation used by SIRIUS to determine SEP is:

$$SEP = \sqrt{\frac{\sum_{i=1}^{n}(\hat{yi} - yi - bias)^2}{n-1}} \quad (2)$$

where:

$\hat{yi}$ = the predicted value

yi = the expected (measured) value

$bias$ = the mean of all errors ($\overline{\hat{yi} - yi}$)

n = the number of data points.

The calculation of SEV is very similar to the calculation of SEP; the SEV calculation uses the calibration data set, while the SEP calculation uses the validation data set. A model was deemed acceptable for use if the R^2 coefficient was 0.75 or greater [Kramer, 1998].

Whichever data weighting method was attempted, the model created converged to the same point, that is to say, that a similar model was (generally) created no matter what the initial settings of the program were. It was ultimately determined that dividing each element in the data set by the overall mean of all elements in the data set (divide by mean) was the weighting method that produced the best results. Factors such as the number of principal components, and the number of groups in cross-validation were also changed, but had little effect on the model. The models generated all had 3 or fewer principal components. Identical methods were used to produce both the F1 and F2 models.

3. RESULTS

Table 1 gives a summary of the sampling data sets for F1 and F2, showing the range of the data, together with the means and standard deviations. For both F1 and F2, the minimum emission rates were less than half of the maximum emission rate, which shows that a significant variation in NOx generation was achieved during sampling.

Table 1. Summary of raw data set.

Furnace	No. of Samples	Emission Rate of NOx (g/min)		
		Min.	Mean	Max.
F1	15	406.5	673.1	827.0
F2	52	6.3	9.8	13.3

Tables 2a and 2b give correlation data for the models, for both calibration and validation data sets. This data is often referred to as the 'goodness of fit' measures for the model. SEV and SEP, can be viewed as a good measure of the model fit, as they can effectively be expressed as a model prediction accuracy, e.g. the F1 Model (refer Table 2b column 2) should be able to predict NOx levels to ± 80.5 grams/minute. This value may appear high, however it must be examined with reference to the range of emission rates for the aforementioned stack. Thus the most important column in Table 2b is the 'SEP % of median', which calculates the percentage which SEP contributes to the median emission rate during sampling. This ranges between 9.4% and 13.1% for the two models. It is evident that the R^2 values for all the models are usually quite close to 1, which is ideal. It will also be noticed that the lowest R^2 values do not correspond with the lowest SEV/SEP values. The model equations derived for the two stacks are presented below.

Table 2a. Goodness-of-fit for model calibration

Model	MODEL CALIBRATION		
	SEV	SEV % of med	R^2
F1	41.008	6.6	0.935
F2	0.914	9.3	0.819

Table 2b. Goodness-of-fit for model validation

Model	MODEL VALIDATION		
	SEP	SEP % of med	R^2
F1	80.512	13.1	0.903
F2	0.920	9.4	0.759

The calculated model for the F1 stack is:

$$E_{F1}= -822.074 + 4.394xT_s - 18.473xO_s + 0.176xT_{fa} + 1.127xT_{fb} - 0.016xT_{fc} + 1.572xF_a + 279.932xF_b + 7.705xF_c - 54.279xO_a - 528.276xO_b + 9.406xO_c - 1.743xR_a + 0.006xR_b - 0.128xR_c - 0.011xS_a - 1.224xS_b + 0.162xS_c, \quad (3)$$

where:

E_{F1}	=	NOx emission rate from F1 (g/min)
T_s	=	Stack Temperature (°C)
O_s	=	Stack Oxygen (%-Dry)
T_{fa}	=	F1a Firebox Temp. (°C)
T_{fb}	=	F1b Firebox Temp. (°C)
T_{fc}	=	F1c Firebox Temp. (°C)
F_a	=	F1a Fuel Gas Cons. Rate (Tonnes/day)
F_b	=	F1b Fuel Gas Cons. Rate (T/d)
F_c	=	F1c Fuel Gas Cons. Rate (T/d)
O_a	=	F1a Excess Oxygen (%-Wet)
O_b	=	F1b Excess Oxygen (%-Wet)
O_c	=	F1c Excess Oxygen (%-Wet)
R_a	=	F1a Regen. Flue Gas (T/d)
R_b	=	F1b Regen. Flue Gas (T/d)
R_c	=	F1c Regen. Flue Gas (T/d)
S_a	=	F1a Steam Generation (T/d)
S_b	=	F1b Steam Generation (T/d)
S_c	=	F1c Steam Generation (T/d).

The coefficients are calculated by SIRIUS as part of the PCA model construction.

Figure 1 shows the predicted vs measured graph for the model. The measured data is that obtained from sampling, while the predicted data are values obtained using the above model. The line fitted through the graph shows the spread of values either side of the line. For a perfect model, all the data will be arranged on the line with no 'spread' of data. The greater the amount of deviation from the line, the worse the model.
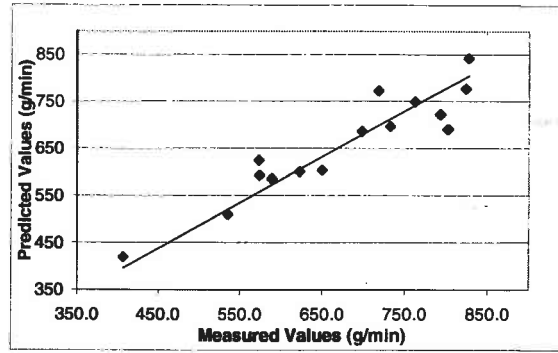

Figure 1. Predicted vs measured plot for F1 model.

The calculated model for the F2 stack is:

$$E_{F2}= 132.522 + 0.148xT_s + 0.153xO_s + 0.009xT_f - 1.228xH + 0.189xF_o + 0.758xF_g - 0.068xT_I - 0.155xT_o, \quad (4)$$

where:

E_{F2}	=	NOx emission rate from F2 (g/min)
T_s	=	Stack Temperature (°C)
O_s	=	Stack Oxygen (% - Dry)
T_f	=	Furnace Firebox Temp. (°C)
H	=	Fuel Gas Hydrogen (Molar %)
F_o	=	Fuel Oil Cons. Rate (T/d)
F_g	=	Fuel Gas Cons. Rate (T/d)
T_I	=	Process Temperature IN (°C)
T_o	=	Process Temperature OUT (°C).

Again the coefficients are generated by SIRIUS using the PCA model fit.

Figure 2 shows the predicted vs measured graph for the F2 model, which shows a reasonable amount of spread to the data, however it is evenly distributed either side of the line. The R^2 values are lower for F2 as compared to F1 (see Tables 2a and 2b).
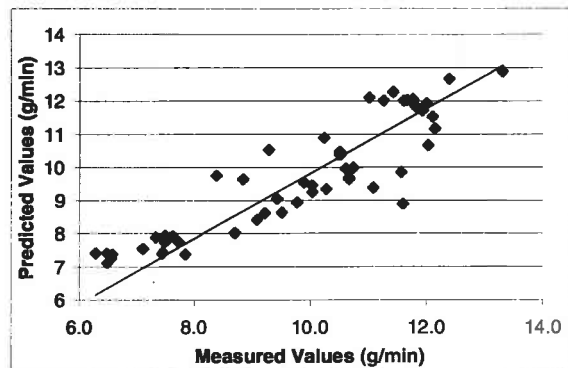

Figure 2. Predicted vs measured plot for F2 model.

4. DISCUSSION

Overall, the R^2 values are all above 0.75, and SEP values for the models (Tables 2a and 2b) are relatively small, suggesting that the models are a good fit to the data. This is further evidenced by the good correlation shown in Figures 1 and 2. The method appears to be quite robust, the data weighting method used (divide by mean) is a standard method and is commonly used. The fact that the data constantly converged to a similar model (in terms of SEP and R^2 values) from a number of different starting points (data weightings, etc.,) points to the accuracy and robustness of the method. It also indicates that the optimum point holds for a wide range of starting values.

The F1 model shows a strong correlation between the parameters for boiler F1b and the overall NOx level, evidenced by the much larger coefficients on model terms for F1b than for F1a or F1c. This is an interesting finding, as it was previously assumed by AOR, that the NOx contribution of the three units would be identical. The strong correlation between boiler F1b and the NOx emission rate, suggests that the boiler is significantly different to the others. Therefore, significant NOx reductions can be gained by altering parameters of boiler F1b only.

A sensitivity analysis of the model was performed, by calculating the model equation for a range of values for each parameter, in order to determine the effect of each individual parameter on the model. The sensitivity analysis indicated that increasing excess oxygen (O_a, O_b, O_c) has the greatest effect on the emission rate of NOx. Using the model, with all 3 boilers in operation, it is possible to reduce the calculated NOx level to 200g/min, with the application of large amounts of excess air. However, this presents 2 problems: firstly, that high quantities of excess air make the process inefficient, thus requiring more fuel to perform the same task (create the same amount of steam), and secondly (and most importantly) the accuracy of the model is insufficient to make such predictions. The model can only be used with an accuracy of ± 80g/min., since that is the magnitude of SEP. The problem this represents is that the lowest value in the data set was approx. 450g/min. Although the model can be used to lower the NOx emission rate to 200 ± 80g/min., the model tolerance becomes unacceptably high. Also, there is some question over modelling a situation for values which are well outside the sampled range. Therefore the F1 Model (3) is accurate within the range of 400g/min (of NOx) and above. Since the normal operating range for the F1 unit is 650g/min or above, this should not present any problems.

For the range of data collected, the maximum NOx emission rate for the F2 stack is approximately double the minimum rate (Table 1). Although some of the difference is due to different firing rates (furnace operational level/rate) producing different flow rates through the stack, much of the variation is evidence of the scope for NOx minimisation through combustion controls.

For the F2 model, there does not appear to be any single factor which correlates strongly with the NOx level. Rather there are a number of factors with a moderate correlation, which in conjunction, will have a significant NOx reduction effect. NOx increases by approximately 0.5g/min for every 100°C increase in furnace temperature (T_f) and approximately 0.5g/min for every 1/2 tonne reduction in fuel gas flow rate ((F_g)-even if this is replaced by 1/2 tonne of oil). It is important to note that the fuel gas flow (F_g) has a higher coefficient, in the model than the fuel oil (F_o), thus the emissions of NOx are more sensitive to F_g than F_o. It is likely that this is due to the high hydrogen content of the gas. Fuel oils would result in higher NOx levels, since most heavy oils contain some nitrogen (1 molar % or less at AOR), and oils are more difficult to combust, generally requiring higher excess air levels.

Figure 2 shows a relatively even distribution of data along the line, with little clumping. However there appear to be some patterns emerging in the deviation from the fitted line. Towards the bottom (left hand) corner of the figure there is a clump of data points above the line, while towards the right hand side there are some points which deviate significantly from the line. This means that the model is unable to accurately predict in these regions. Another possibility is that the processes are not linear.

5. CONCLUSION

From the data given above it has been shown that it is possible to produce acceptable empirical models to predict NOx emissions from refinery furnaces. Technological and other differences between furnaces increase the complexity of the process, necessitating a greater number of models than would otherwise be required.

The variables used in the models to predict NOx are those which are readily obtainable to AOR from their telemetry systems, thus allowing calculation of the model to be simple and straightforward.

The models are able to predict NOx emissions over the range of NOx values sampled, with acceptable accuracy (usually 15% or less error). The model accuracy appears to degrade when predictions are outside the range of sampled values.

Minimisation of NOx emissions by the use of combustion control methods has proven to very effective, allowing average NOx reductions of 50% to be easily achievable. However, in practice, the main impediment to NOx reduction is the inflexibility of process operating parameters. Many of AOR's process units do not have sufficient scope to incorporate NOx reduction measures. Substitution of the hydrogen in the fuel with carbon compounds would be advantageous. This option is not presently possible at AOR.

The advantages of the production of models such as these, are their ability to be incorporated into refinery operating systems, allowing NOx levels to be continually managed and minimised. This ensures that licence conditions will be continually met and environmental impacts minimised (even with a rapidly changing process), without the need for the installation of expensive monitoring equipment.

The modelling was made possible due to the strong correlation between operating conditions and the NOx emission rate. Therefore, the methodology presented in this paper would also be suitable for modelling other emissions which are strongly dependant on process conditions.

6.   ACKNOWLEDGEMENTS

7.   REFERENCES

Cheremisinoff, P., (ed.) *Air Pollution Control and Design for Industry*, Marcel Dekker, Inc., New York, 1993.

De Nevers, N., *Air Pollution Control Engineering*, McGraw-Hill, Inc., New York, 1995.

Hesketh, H., *Air Pollution Control - Traditional and Hazardous Pollutants*, Technomic Publishing Company, Inc., Pennsylvania, 1991.

John Zink Company, *NOx Control in Fired Heaters*, American Institute of Chemical Engineers, Winter National Conference, Georgia, 1984.

Kramer, R., *Chemometric Techniques for Quantitative Analysis*, Marcel Dekker, Inc., New York, 1998.

Lear Siegler, *Enerac 3000 Instruction Manual*, Lear Siegler Australasia, Pty. Ltd., Sydney, 1995.

Lixing, Z., *Theory and Numerical Modelling of Turbulent Gas-Particle Flows and Combustion*, Science Press, Beijing, 1993.

Massart, D., B. Vandeginste, S. Deming, Y. Michotte, and L. Kaufman, *Chemometrics: A Textbook*, Elsevier Science Publishers, Amsterdam, 1988.

Wight, G. *Fundamentals of Air Sampling*, CRC Press, Florida, 1994.

Xu, M., Y. Fan, and J. Yuan, *Combustion Science and Technology Journal* 133(4-6), 377-394, 1998.