SPE-177468-MS

First Principle Models for Emission and Performance Monitoring

Jan Sandvig Nielsen, Weel & Sandvig
Mogens Weel, Weel & Sandvig

This paper was prepared for presentation at the Abu Dhabi International Petroleum Exhibition and Conference held in Abu Dhabi, UAE, 9–12 November 2015.

Introduction

Combustion processes such as gas turbines, furnaces, flares and boilers in the oil and gas industries are significant sources of pollutants that can impair human health and the environment, including sulfur dioxide (SO2), nitrogen oxide (NOx) and carbon monoxide (CO). Further, these sources will have an impact on global climate via its emission of greenhouses gases – primarily carbon dioxide (CO2).

SO2 and NOx, when emitted to the air, react with water and other compounds to produces various forms of acidic compounds and particles, which can remain in the air for days or weeks. Depending on wind direction and speed, these harmfull substances can be spread in wide areas and are not necessarily limited to the country of the emission sources. When the pollutants fall on to earth or water they will have impact on air quality, visibility, acidification, sensitive forest and coastal ecosystems.

SO2 and NOx emissions form fine particles in the atmosphere. Particulate matter is the term used for a mixture of solid particles and liquid droplets found in the air; fine particles (PM2.5) are smaller than 2.5 microns (millionths of a meter) in diameter. The gas fired combustion sources emit particles directly into the air, but their major contribution to particulate matter air pollution is emissions of SO2 and NOx, which are converted into sulfate and nitrate particles in the atmosphere. These particles make up a large part of the fine particle pollution in most parts of the country. It is scientifically well recognized that there is a correlation between elevated fine particulate matter and increased incidence of illness and premature mortality. In addition, NOx and organic volatile compounds forms ozone with the presence of sunlight. This ozone will be present at ground level and is a major part of the smog and is also linked to potential health hazards including respiratory illness.

For the same reason, regulators around the world has focused on controlling these kind of emissions by setting maximum permissible emission limits. For larger emission sources it is further requested that companies install and maintain continuous emission monitoring systems.

Until recently, continuous emission monitoring was always done by a set of physical gas analyzers typically in extractive systems, where stack gasses are extracted from the stack and send through heated hoses to the analyzer shelter where the measurements take place. To work correctly the analyzers typically require on-line calibration gasses to maintain acceptable analyzer accuracy. All in all the hardware based continuous emission monitoring systems (CEMS) are complex and costly to install and in particular to keep in good shape.

The complexity of installing and operating hardware CEMS has been one of the motivating factors for introudcuing alternative software based CEMS and since the early nineties a new kind of CEMS has been introduced to the market. These systems are all defined as *Predictive Emission Monitorings Systems* or in short PEMS. They were initialy adopted as approved alternative CEMS by the US Environmental Protection Agency and are now accepted in an increasing number of countries around the world and is now the preferred technology for continuous emission monitoring for gas turbines, boilers and furnaces in organizations like ADNOC and Saudi Aramco. PEMS has proven to be a reliable, accurate and cost efficient alternative to hardware CEMS.

In short, a PEMS is using a mathematical model to correlate indirect measurements such as fuel flow, temperatures and pressures to emissions such as NO_x and SO_2. To build such mathematical correlations it is necessary to understand the fundamentals of emission formation.

Emission formation

Harmful emissions from combustion processes can, to a wide extend, be divided into two classes: *Stoichiometric emissions* – dictated alone by the composition of the fuel and *rate formation emissions* – where emission formation is depending on the conditions in the combustion process. To the first group belongs the formation of SO_2 and CO_2 and to the other NO_x and CO.

For example, the emission rate of SO_2 is depending only of total Sulphur content of the fuel and the fuel flow rate, assuming 100 % conversion rate. The SO_2 concentration is additionally dependent on the combustion airflow rate.

The rate formation emissions, on the other hand, is dependent on the combustion process itself. The reaction rate is typically dependent on both residence time, temperature and reactants and products concentrations.

For NO_x emissions (sum of NO and NO_2 and calculated as NO_2) the mechanisms are very complex.. While the details are beyond the scope of this paper a few key mechanism will be described to illustrate the complexity and to illustrate the importance of understanding the fundamentals when building the PEMS models. A good detailed description of NO_x can be found in (R. Miller et al. 1998).

NO_x formation in combustion processes can with reasonable accuracy be simplified to four basic reaction mechanisms or routes:

1. Thermal NO_x – extended Zeldovich mechanism
    a. $O_2 \rightarrow 2O$
    b. $N_2 + O \rightarrow NO + N$
    c. $N + O_2 \rightarrow NO + O$
    d. $N + OH \rightarrow NO + H$

At high temperatures, molecular nitrogen (N2) and oxygen (O2) in the combustion air disassociate into their atomic states and participate in a series of reactions known as the Zeldovich mechanism shown above. Each reaction has its own reaction rate that is highly temperature dependent. In general, the NO_x formation rate will be exponential with temperature, following a typical Arrhenius kinetic reaction model.

2. Prompt NO_x

Under certain conditions, NO is found very early in the flame region—a fact that is actually in conflict with the idea of a kinetically controlled process. It is assumed to be caused by fuel derived radicals and will create free Nitrogen that will react with oxygen and create NO. This is not dependent on residence time but highly on temperature like the Zeldovich mechanism.

3. Fuel NO_x

High temperature reaction of organic bound Nitrogen in the fuel. This is most typical for solid fuels like coal and biomasses.

4. Nitrous oxide NO_x

Finally under higher pressure N2O – laughing gas – can be formed and decompose into NO.

Some of the above mechanisms are dominant is some applications while some are in others. For example, Fuel NO_x is playing a minimal role in most gasfired application, but can play a significant role in biomass boilers and waste incineration plants.

First Principle PEMS

An accurate and reliable predictive emission monitoring system (PEMS) must be able to capture the major mechanisms affecting the emission formation. Following the above description of major NO_x formation routes, it is evident that temperature and plays an important role. For most PEMS applications the thermal NO_x route (Zeldowich) is dominating, counting for 80-95 % of the NO_x formation.

Each of the reactions constituting the Zeldowich mechanism has it owns kintect reaction parameters, but overall the raction rate is exponential with the temperature. Knowing this, it is evident that the highest NO_x formation takes place in the flame zone, where the combustion temperature is at its highest level. Very simplified the NO_x reaction rate in this zone can be expressed as

$$NO_x\left(\frac{mole}{s}\right) = F_1 e^{T_{flame}\,F_2}$$

were F1 and F2 are functions of combustion pressure, O_2 partial pressure, reseidence time etc.

These parameters are dependent of the specific combustor geometry. They can not easily be derived analytically and for practical use the above equation will typically be replaced with one in the form

$$NO_x\left(\frac{mole}{s}\right) = NOx_{ref}\,e^{\frac{T_{flame}\,F_P - T_{ref}}{c}}\,F_{Tresidence}\,F_{comp}$$

were

NOx_{ref}	is formation rate at refence point
T_{ref}	is flame temperature at refence point
F_p	is correction factor as function combustion pressure and reference combustion pressure

c is a model constant
$F_{Tresidence}$ is a correction factor based on relative residence time
F_{comp} is a correction factor based on air composition relative to reference point

With this type of equation, we are are looking at relative changes based on reference values. It is evident that the reaction rate is exponential but the exact curvature is depending on various the actual burner design.

In practice, the above formula type can be used to establish a NOx characteristic curve for the specific emission sources based on few reference measurements. This is illustrated in Figure 1 were several possible NOx rates are shown in dotted line and where reference measurements are used to find the exact line that is valid for the given combustion source.

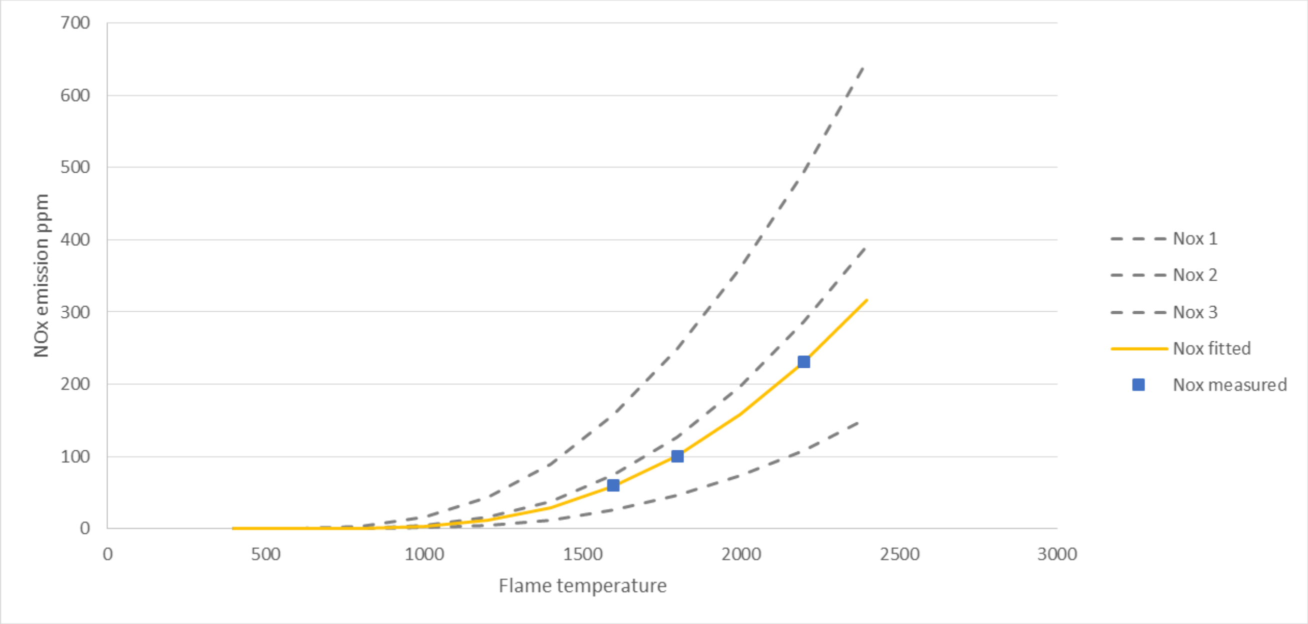


Figure 1 Defining NOx characteristic curve – NOx as function of flame temperature

The flame temperature, is not directly measurable, but is in turn depending on the fuel flow, air flow, combustion air temperature, pressure, humidity and more. For most industrial emission sources also air flow measurement is unavailable.

To calculate the flame temperature needed for NOx estimation, *first principle models* are using energy and mass balances coupled with equipment performance curves, to calculate the actual conditions in the combustion zones.

To illustrate the basic approach a gas turbine with free power turbine is used (see Figure 2). Air is compressed in the compressor (Satge 2 to stage 3). The compressed air is mixed with fuel and burned in the combustion chamber (stage 3 to 4) and enters the high pressure turbine (stage 41). The high pressure turbine is powering the compressor (expanding combustion gas from stage 41 to stage 44). The combustion gas finally expand in the power turbine (stage 45 to 5) producing shaft power that can be converted to electricity production or used for mechanical drive.

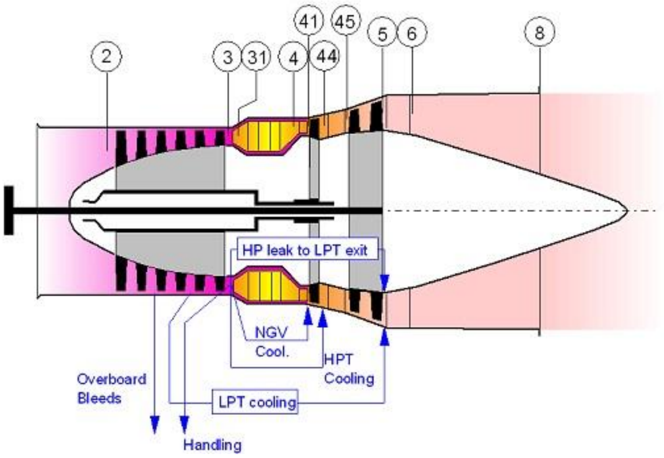


Figure 2 Gas turbine stages: 0: ambient, 1: Inlet, 2: Compressor inlet, 3: Compressor exit, 4: Combustor outlet, 45: Power turbine inlet, 5: Turbine outlet. (from GASTURB – Kurzke 1998).

As energy and mass balances is applied to calculate the conditions of the unmeasured stages such as the combustion stage (stage 4) and the assoiciated flame temperature that is a key parameter in NOx calculation. Additional equipment performance curves are applied to give redundancy in the data enabling data validation and input data reconciliation.

For the sample gas turbine the following balances are available:

- Global energy balance
- Core engine shaft power balance
- Power turbine shaft power balance
- Global mass balance

In addition, performance curves and balances are available for key components:

- Compressor maps
- Turbine maps / flow functions (High pressure turbine, power turbine)

In a compressor, the mass flow rate and compressor efficiency is governed by the shaftspeed, inlet pressure, inlet temperature and air composition.

The basic calculation sequence is initially to estimate the air flow rate through the gas turbine. Then based on air flow the state conditions (flow, temperature and enthalpy) can be calculated using energy and mass balances stage by stage through the gas turbine – Ambient -> Compressor -> Combustor -> turbine -> exhaust. The calculation sequence is outlined in Figure 3.

In additional to the stage by stage mass balances, other balances or preformnce curves can be applied to check the validity of the input sensors. If the measurements are error free the additional balances should show no deviation, but in reality all industrial sensors have a limited accuracy and are prone to failure or drift. The additional set of model equations can thus be used to describe the quality of the input data set and subsequently used to estimate the expected “real” sensor values.

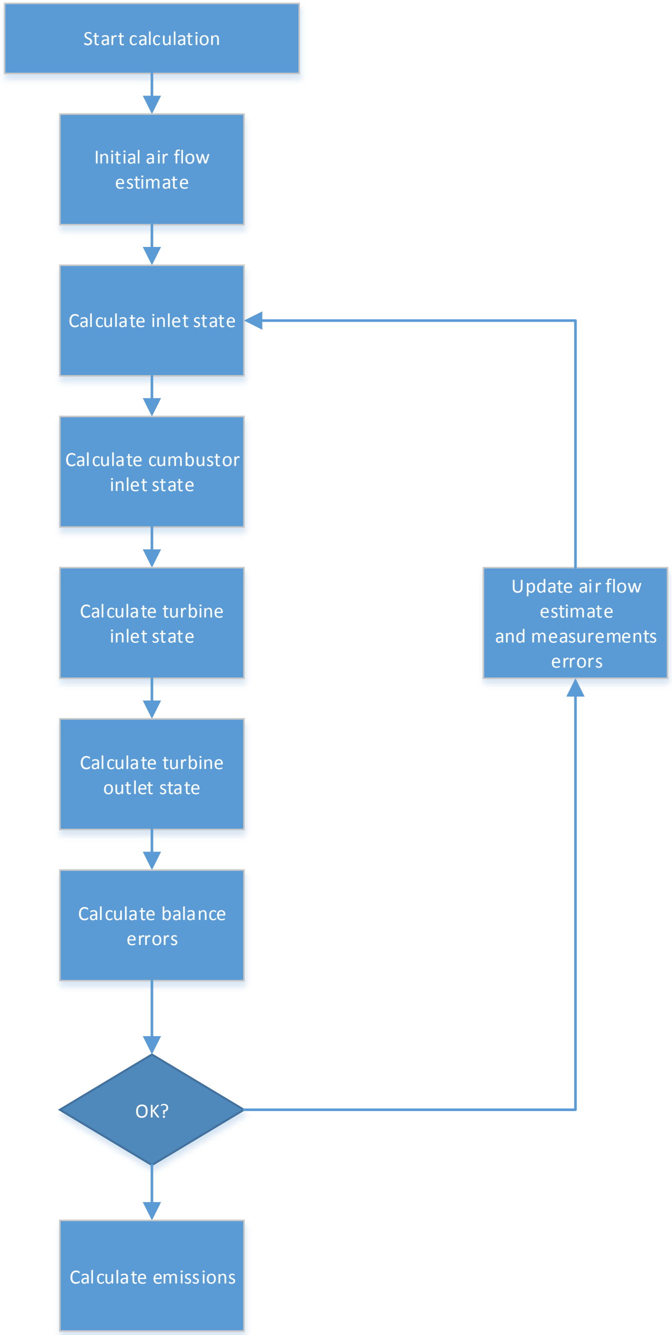
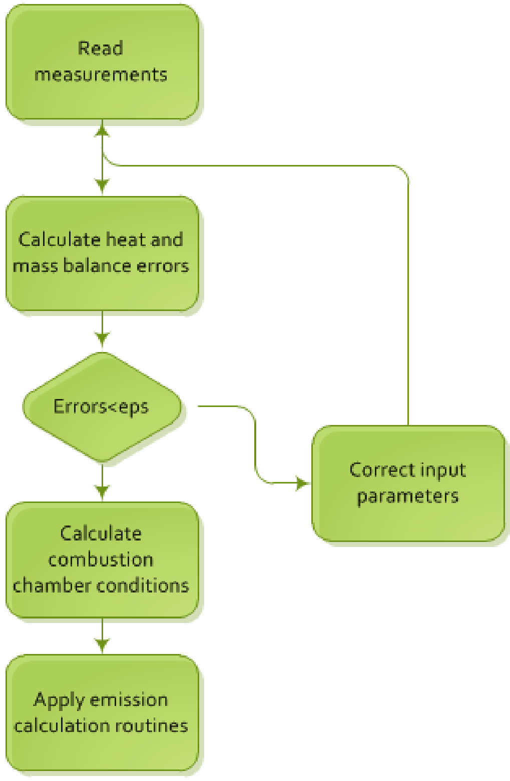


Figure 3 Overall calculation sequence

The ability to quality check input values is a key to have a reliable and robust PEMS model.

In First Principle PEMS, data validation and data integrity check is carried out on-line in two steps. The first step is a simple range check where all sensor signals are checked against the expected range. Outliers are flagged as failed measurements.

In the second stage of the data validation process, sensor signals are tested against known physical relations including energy and mass balances. The key in this test is to estimate the sensor signal error for each used signal in a way that the basic energy and mass balances are fulfilled. The real process



value X_i is then defined by $X_i = X_{m,i} + \Delta X_i$ where $X_{m,i}$ is the measured value and ΔX_i is the correction/error value.
In first principle PEMS the most likely set of correction values are found via an inline optimization routine that minimizes the objective function:

$$obj = \min\left(\sum_i (\Delta x_i \cdot weight_i)^2 + \sum_j \left(\Delta\omega_j \cdot weight_j\right)^2\right)$$

$$\Delta x_i \; measurement\ error$$

$$\Delta\omega_j \; balance\ error\ (mass\ and\ energy)$$

Weight factors are based on the individual sensors accuracies and on the effect on energy and mass balances.
This on-line data reconciliation minimizes the direct effect of incorrect sensors.

PEMS Sensitivity analysis and uncertainty assessment

During installation a sensitivity test is conducted where each input parameter is artificially modified and the effect on predicted emission is calculated. This could for example be the fuel gas flow rate where we in the sensitivity analysis are artificially changing the measured value by 5 % and then recording the effect on NOx emission (flow rate and or concentration).
The sensitivity is calculated as $w_{c,i} = \frac{\Delta E_c}{\Delta S_i}$ where ΔE_c is the change in emission parameter c and ΔS_i is the change in sensor signal on sensor i.

Total uncertainty realted to sensors signal errors can can be estimated based on the sensitivity parameters $w_{c,i}$.

$$U_c = \sqrt{\sum_i \left(U_i \cdot w_{c,i}\right)^2}$$

where U_c is the calculated uncertainty on emission value c and U_i is the uncertainty on sensor i and $w_{c,i}$ is the sensitivity on emission parameter c relative to sensor i.

First principle versus data driven PEMS

The PEMS models available is basically divided into two groups of systems. The first principle approach as described above and the data driven approach, that is based on black box model relating input data with known outputs (emissions).

In data driven models known relations such as energy and mass balances are basically discarded. Instead, a statistical method for relation input signals with output signals is used – typically based on

neural networks.
In a neural network the relation between inputs and outputs are generated through a number neuron layers. In each neuron layer there is a number of neurons that are connected with each neuron in the previous layer and the next layer. Each connection is having a weight that is used for the network calculation.

The fundamental idea in a neural network is to find the right weights for the connections. This is done by "training" the network with input values and known output values. To be accurate the neural network has to be trained over the complete operating envelope (combination of input signals).

The important part of setting up a neural network is to define which input signals should be included in the network. Especially parameters with small variation during training can be dangerous to include. For that reason it is necessary to train the network under different weather conditions, different load levels, different fuel composition etc. to have an accurate PEMS system.

The major advantage of data driven models is that they apparently does not need any knowledge of the system they are applied on. Model development is relatively limited.

On the downside is the need for training. To have a decent data driven PEMS system that works under all conditions it is basically required that calibration measurements are done under various operation condition including winter and summer operation. Unfortunately this is rarely done.

The first principle models on the other hand are requiring more modeling work. Each model needs to be configured according to the specific source configuration and input signals availability. In practice first principle PEMS is having an extensive library of models for specific combustion sources and for different collection of available input signals.

The major advantage of the first principle models is that they exploit the physical facts and use their relations in the model. There is therefore significant less calibration measurements required compared with data driven based systems.

It is important to emphasize the fact that data driven methods are discarding all the valuable information available in the physical relations.

Overall, it is recommended to use first principle PEMS models whenever it is possible to build explicit model of the emission source and use data driven PEMS models this is not possible.

First principle PEMS results

First principle PEMS has been installed on a large number of emission sources including furnaces, gas turbines and boilers. The PEMS solutions has been used for environmental compliance (eg. After US EPA or European regulation) as well as for environmental taxation (e.g. NOx taxes in Europe).

To demonstrate compliance, the installed PEMS system is validated against reference measurements – typically done by certified third party accredited institute. The specific procedure for validating the PEMS differs from country to country, but broadly follow either US EPA 40 cfr Part 16 (performance specification 16) or European standard EN14181 (QAL2 test).

Samples of validation tests is shown in Figure 4 (NO_x) and Figure 5 (CO). The tests were done after US

EPA performance specification 16 with relative accuracies well within the acceptance range.

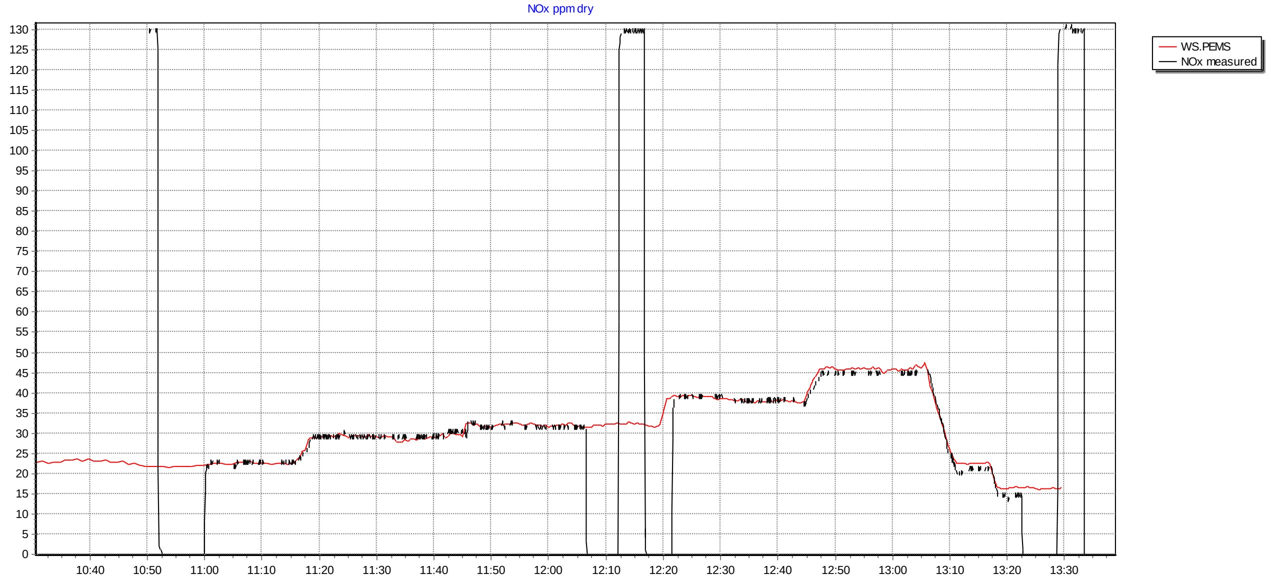


Figure 4 PEMS validation – PEMS reading (red line) versus reference measurements (black line). High and zero level reference measurements are not real measurements, but is reflecting zero and span check of instrument used for reference measurements.

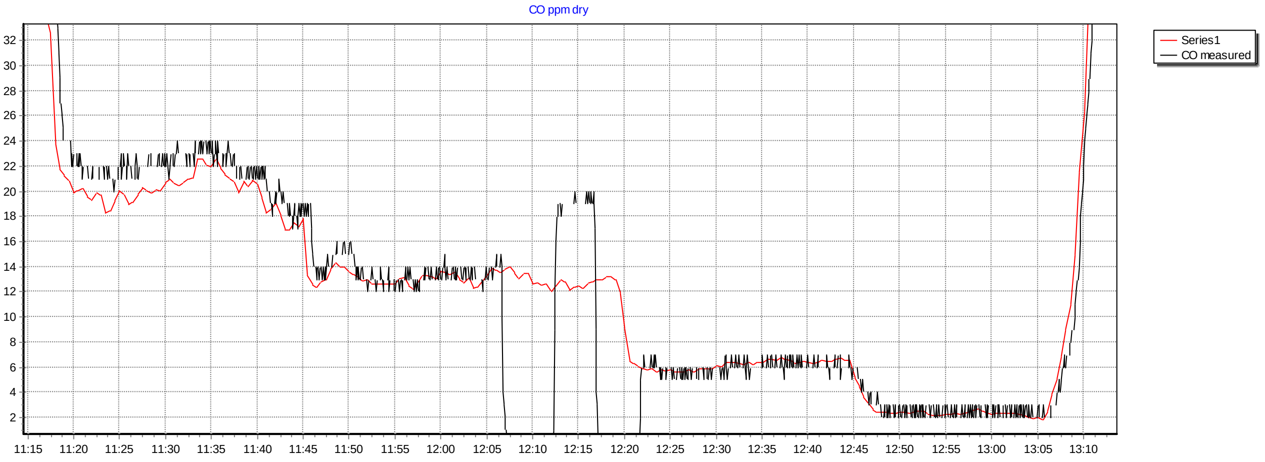


Figure 5 PEMS validation CO - PEMS reading (red line) versus reference measurements (black line). High and zero level reference measurements are not real measurements, but is reflecting zero and span check of instrument used for reference measurements.

Performance monitoring

In the First Principle PEMS model, we continuously calculate energy and mass balances and reconcile input data. With little additional effort, it is possible to extend the PEMS model with a valuable performance-monitoring module.

Even under the best possible operating conditions, the performance of energy conversion plants (boilers, furnaces, gas turbines etc.) are subjected to deterioration over time.

For a gas turbine the degradation is due to compressor fouling and corrosion, inlet filter clogging, thermal fatigue and oxidization of hot-gas path components such as combustion liners and turbine blades. The performance degradation attributed to compressor fouling is mainly due to deposits formed on the compressor blades by particles carried in by the air that are not large enough to be catched by the inlet filter. Depending on the environment, these particles may range from dust and soot particles to water droplets or even insects. Such deposits result in a reduction of compressor mass flow rate, efficiency and pressure ratio which in turn causes a drop in gas turbine's power output.

This type of degradation is the most important. Indeed, several studies of heavy-duty industrial gas turbines suggest that the decrease in output can easily reach 5% after a month's operation (e.g. Diakunchak, 1992).

However, compressor fouling is a "recoverable" degradation. Periodic on-line and off-line compressor washes will restore the performance – at least partially. In an on-line wash, distilled water is injected into the compressor while the gas turbine is running such that water droplets impact the blades at high speeds to loosen and partially remove deposits. This will, however, only recover some of the performance. Full recovery can only be achieved by an off-line wash where distilled water (sometimes mixed with a special detergent) is sprayed into the gas turbine while being rotated by the starter at the crank speed.

Inlet filter clogging is another cause for reduced performance. It reduces gas turbine air flow and compressor inlet pressure and thus badly affects gas turbine performance. Replacing the old filter with a new one can recover the lost performance.

As opposed to the recoverable performance lossess, the performance degradation associated with hot gas path components is mostly non-recoverable. To get full recovery for these losses an engine overhaul is required.

All measures for recover performance is having an associated cost. Therefore, there need to be a balance between the lost performance and the cost of restoring performance. A good maintenance plan is essential and with a performance monitoring system it is possible to schedule the frequency of wash (online as well as offline) and filter replacement, based on specific charecteristics of the turbine.

The main step in the performance monitoring system is to determine the difference between actual performance and what could or should be the performance when the engine is new and clean.

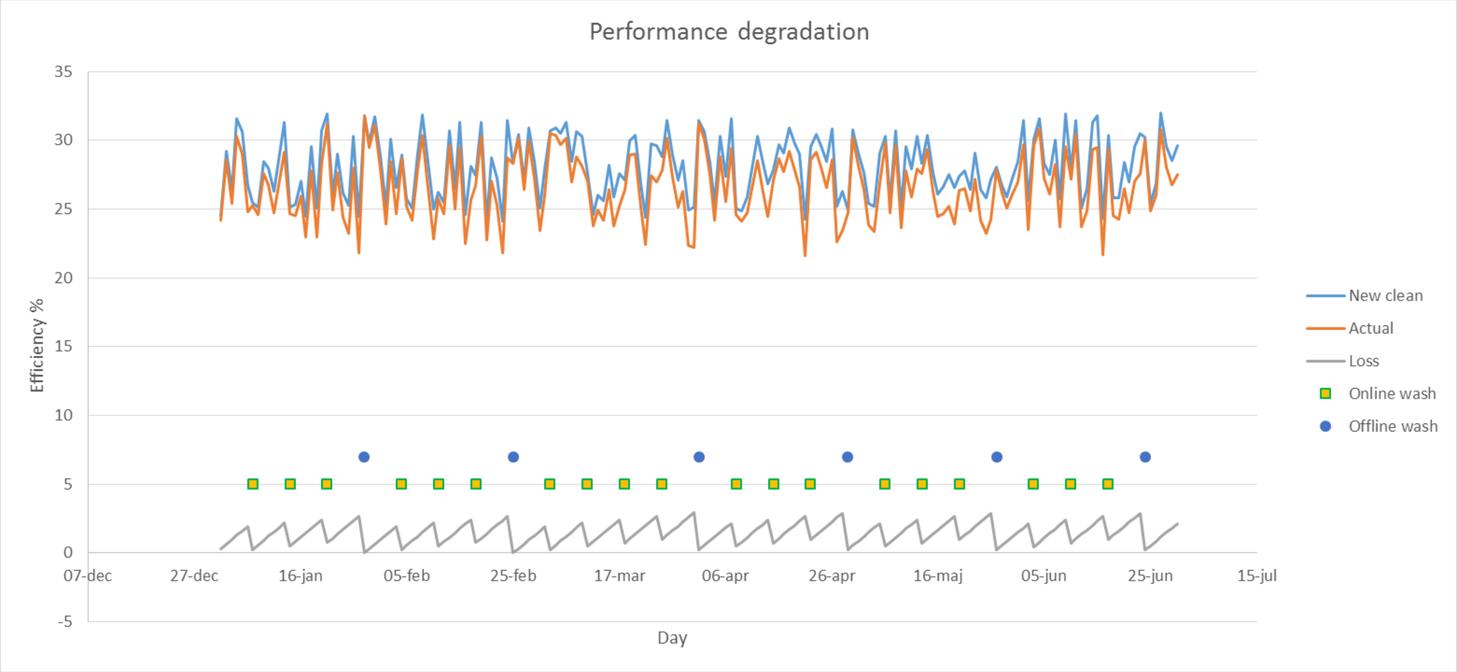


Figure 6 Performance degradation –turbine with scheduled online and offline wash.

The drop in efficiency is directly proportional to energy loss in a single cycle gas turbine. For a 50 MW gas turbine operating 7000 hours per year 1 % average improvement will produce 3500 MWh more per year. With a power price of 70 USD/MWh this will given an annual saving or revenue of 245 000 USD/yr.

Performance monitoring can also be added as additional modules for other processes. A simple example is from a industrial furnace application were the first principle PEMS model was installed. The furnaces was old and not equipped with oxygen sensors. Instead the PEMS application was including O_2 calculation and this output together with flue gas temperature and gas composition can be used to calculate the furnace efficiency. The baseline operation turned out to be with 11 % O_2 and 260 deg C stack temperature giving a thermal efficiency of 80 %. Reducing the oxygen surplus and the stack temperature will increase the furnace efficiency – see Figure 7 where also the efficiency improvement by changing the operating parameters can bee seen.

Efficiency table Stack temperature

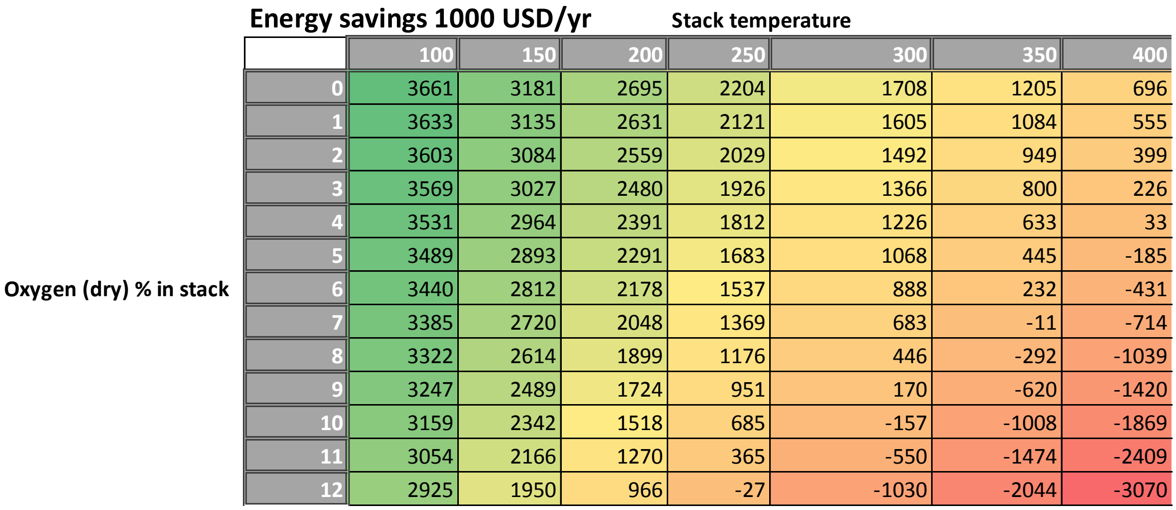
80.07	100	150	200	250	300	350	400
0	95.93	93.85	91.75	89.62	87.47	85.29	83.08
1	95.81	93.65	91.47	89.26	87.02	84.76	82.47
2	95.68	93.43	91.16	88.86	86.53	84.18	81.80
3	95.53	93.18	90.81	88.41	85.99	83.53	81.05
4	95.37	92.91	90.43	87.92	85.38	82.81	80.21
5	95.18	92.60	89.99	87.36	84.69	82.00	79.27
6	94.97	92.25	89.50	86.72	83.92	81.07	78.20
7	94.73	91.85	88.94	86.00	83.03	80.02	76.98
8	94.46	91.39	88.29	85.16	82.00	78.80	75.57
9	94.14	90.85	87.54	84.19	80.80	77.38	73.92
10	93.76	90.22	86.64	83.03	79.39	75.70	71.97
11	93.30	89.45	85.57	81.65	77.69	73.68	69.63
12	92.74	88.52	84.25	79.95	75.60	71.21	66.77

Efficiency improvement Stack temperature

	100	150	200	250	300	350	400
0	15.86	13.78	11.68	9.55	7.40	5.22	3.01
1	15.74	13.58	11.40	9.19	6.96	4.69	2.40
2	15.61	13.36	11.09	8.79	6.47	4.11	1.73
3	15.46	13.12	10.74	8.35	5.92	3.47	0.98
4	15.30	12.84	10.36	7.85	5.31	2.74	0.14
5	15.11	12.53	9.93	7.29	4.63	1.93	-0.80
6	14.91	12.18	9.44	6.66	3.85	1.01	-1.87
7	14.67	11.78	8.87	5.93	2.96	-0.05	-3.09
8	14.39	11.32	8.23	5.10	1.93	-1.27	-4.50
9	14.07	10.79	7.47	4.12	0.74	-2.69	-6.15
10	13.69	10.15	6.58	2.97	-0.68	-4.37	-8.10
11	13.23	9.38	5.50	1.58	-2.38	-6.39	-10.44
12	12.67	8.45	4.19	-0.12	-4.46	-8.86	-13.30

Figure 7 Performance Industrial Furnace – Efficiency table (Lower Heating Value) and efficiency approval table as function of excess oxygen content in stack and stack temperature.

The improvement can be translated into annual savings based on average fuel price and operating hours (Figure 8). As noted, the savings can be significant. Achieving 5 % excess oxygen in stack should be readily possible – giving an annual saving in fuel costs of more than 1.5 MUSD/yr.



Energy savings 1000 USD/yr **Stack temperature**

Oxygen (dry) % in stack	100	150	200	250	300	350	400
0	3661	3181	2695	2204	1708	1205	696
1	3633	3135	2631	2121	1605	1084	555
2	3603	3084	2559	2029	1492	949	399
3	3569	3027	2480	1926	1366	800	226
4	3531	2964	2391	1812	1226	633	33
5	3489	2893	2291	1683	1068	445	-185
6	3440	2812	2178	1537	888	232	-431
7	3385	2720	2048	1369	683	-11	-714
8	3322	2614	1899	1176	446	-292	-1039
9	3247	2489	1724	951	170	-620	-1420
10	3159	2342	1518	685	-157	-1008	-1869
11	3054	2166	1270	365	-550	-1474	-2409
12	2925	1950	966	-27	-1030	-2044	-3070

Figure 8 Cost savings chart showing the potential savings from modifying excess oxygen and temperature at stack.

Summary and conclusion

First principle PEMS models are based on physical realtions between plant operating parameters and emission of harmful substances such as NO_x, CO and SO_2. These models are well matured and is a cost effective alternative to tradition analyzer based CEMS systems.

The first principle PEMS has a significant advantage over the data drieven PEMS in terms of accuracy in an extended operation range and with the option of combining it with performance monitoring module.

The combined emission and performance monitoring system will thus not only fulfilling environmental regulation but will also help the end user to increase plant efficiency and thus profitabililty.

First principle PEMS has been used in various applications (Furnaces, Boilers, Gas Turbines, Flares and gas engines) onshore as well as offshore. The models has demonstrated very high accuracies and provided valuable feedbacks to end users in terms of operating guidances.

References

R. Miller, G. Davis, G. Lavoie, C. Newman and T. Gardner, “A SuperExtended Zeldovich Mechanism for NOx Modeling and Engine Calibration”, SAE, (1998)

Kurzke, Joachim, 1998, GasTurb 8.0 “A Program to Calculate Design and Off-Design Performance of Gas Turbines,” http://www.gasturb.de/

I. S. Diakunchak , “Performance Deterioration in Industrial Gas Turbines”J. Eng. Gas Turbines Power 114(2), 161-168 (1992)