

WHEN YOU NEED TO BE SURE

SGS

CyFlex® Knowledge Article

Calculating Stack NO_x Emissions using EPA Method 19

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Background

US EPA Method 19 is the official method for calculating stack NO_x emissions when a Continuous Emissions Monitoring System (CEMS) is used to measure CO₂ and NO_x concentrations. For those used to calculating NO_x emissions using 40 CFR 89 or 40 CFR 1065 methods, it is not immediately obvious that Method 19 calculations will give a reasonable result. This paper attempts to demonstrate that the methods will produce equivalent results for a given set of assumptions that are not totally unrealistic. No attempt is made to explain the original thought process that led to the form of the Method 19 calculations. Only the equations involving NO_x and CO₂ are examined.

Basic Fuel Specific NO_x Calculation

For lean equilibrium combustion of dry, CO₂ free air and a pure hydrocarbon with a molar hydrogen to carbon ratio, α , it can be shown (ref) that fuel specific NO_x is given by

$$fsNO_x = \frac{m_{NO_x}}{m_{fuel}} = \frac{y_{NO_x}}{y_{CO_2}} \frac{M_{NO_x}}{M_C + \alpha M_H} \quad \text{pt.1}$$

where m is mass, y is concentration and M is the molecular weight of the subscripted substance. Our assumption of lean equilibrium combustion means that all the fuel carbon will end up as CO₂. If a significant amount of carbon ends up in the exhaust as CO or unburned hydrocarbons, the sum of the concentrations will need to be used in the denominator.

Since the concentrations are in moles of substance per mole of exhaust, it does not matter if the concentration measurement is made on a wet or dry basis as long as both are made on the same basis. So

$$fsNO_x = \frac{m_{NO_x}}{m_{fuel}} = \frac{n_{NO_x}}{n_{CO_2}} \frac{M_{NO_x}}{M_C + \alpha M_H} \quad \text{pt.2}$$

where n is the number of moles of the subscripted substance.

Method 19 Equations

According to Section 12.2.4 of Method 19, given the CO₂ concentration measured on a dry basis, %CO_{2d}, and the pollutant concentration, C_d , the emissions rate, E , of that pollutant is given by Equation 19-6:

$$E = C_d F_c \frac{100}{\%CO_{2d}} \quad \text{pt.3}$$

where E has the English units [lb/million Btu] and %CO_{2d} has units of [%]. According to Section 12.3.2.1, Equation 19-15, the F factor, F_c , which is the volume of combustion components per unit of heat content in [scf/million Btu], is given by

$$F_c = \frac{K(K_{cc} \%C)}{GCV} \quad \text{pt.4}$$

where K is a conversion factor of 10^6 [Btu/million Btu], K_{cc} is a constant of 0.321 [(scf/lb)/%], $\%C$ is the weight fraction of carbon in the fuel in [%] and GCV is the gross calorific value of the fuel in [Btu/lb].

Combining the previous two equations gives us

$$E = C_d \frac{K(K_{cc} \%C)}{GCV} \frac{100}{\%CO_{2d}} \quad \text{pt.5}$$

If we assume the pollutant of interest is NOx, we can rearrange this equations to calculate fuel specific NOx

$$fsNO_x = E \frac{GCV}{K} = C_{NO_x} (K_{cc} \%C) \frac{100}{\%CO_{2d}} \quad \text{pt.6}$$

One of the confusing aspects of Method 19 is the fact that the pollutant concentration is typically measured in [ppm], but the specified units for these equations are [lb pollutant/scf exh]. Table 19-1 provides a [ppm] to [lb pollutant/scf exh] “conversion” factor that is different for each species. Using NOx as an example, we can derive the “conversion” factor by considering that the mass of NOx is related to the number of moles of NOx by

$$m_{NO_x} = n_{NO_x} M_{NO_x} \quad \text{pt.7}$$

and the standard volume of a mole of ideal exhaust gas is given by

$$V_{std,exh} = n_{exh} \frac{R_u T_{std}}{P_{std}} \quad \text{pt.8}$$

where R_u is the universal gas constant, T_{std} is the standard absolute temperature and P_{std} is the standard absolute pressure. So, if we define the “conversion” factor for NOx as Z , we can show that

$$C_{NO_x} = \frac{m_{NO_x}}{V_{std,exh}} = \frac{n_{NO_x} M_{NO_x}}{n_{exh} \frac{R_u T_{std}}{P_{std}}} = Z y_{NO_x, ppm} \quad \text{pt.9}$$

The NOx concentration in ppm, $y_{NO_x, ppm}$, is related to the mole ratio of NOx to exhaust by

$$y_{NO_x, ppm} = \frac{n_{NO_x}}{n_{exh}} \times 10^6 \quad \text{pt.10}$$

By combining the above two equations we can show that

$$Z = \frac{M_{NO_x} P_{std}}{R_u T_{std}} \times 10^{-6} \quad \text{pt.11}$$

Table 19-2 lists standard conditions as 68 [F] and 29.92 [in_Hg]. We can verify that the “conversion” factor matches the value of 1.194×10^{-7} in Table 19-1 by computing

$$\begin{aligned}
 Z &= M_{NO_x} \frac{P_{std}}{R_u T_{std}} \times 10^{-6} \\
 &= 46 \text{ [lb } NO_x \text{ / lb mole } NO_x \text{]} \frac{29.92 \text{ [inHg]}}{1545.3 \text{ [ft lbf / lb mole exh / R]} \times (459.67 + 68) \text{ [R]}} \\
 &\quad \times 144 \text{ [in}^2 \text{ / ft}^2 \text{]} \times 0.48977 \text{ [lbf / in}^2 \text{ / inHg]} \times \frac{1 \text{ [lb mole } NO_x \text{]}}{1 \text{ [ppm } NO_x \text{]}} \\
 &= 1.190 \times 10^{-7} \text{ [lb } NO_x \text{ / scf exh / ppm } NO_x \text{]}
 \end{aligned}$$

pt.12

This is a close enough match to the Table 19-1 value to give us confidence that we properly understand the “conversion” factor.

If we substitute the identities

$$C_{NO_x} = Z \frac{n_{NO_x}}{n_{exh}} \times 10^6 = M_{NO_x} \frac{P_{std}}{R_u T_{std}} \frac{n_{NO_x}}{n_{exh}} \quad \text{pt.13}$$

$$\frac{100}{\%CO_{2d}} = \frac{100}{\frac{n_{CO_2}}{n_{exh}} 100} = \frac{n_{exh}}{n_{CO_2}} \quad \text{pt.14}$$

and

$$\%C = 100 \frac{M_C}{M_C + \alpha M_H} \quad \text{pt.15}$$

into the formula for fuel specific NOx derived from Method 19, we get

$$\begin{aligned}
 fsNO_x &= C_{NO_x} (K_{cc} \%C) \frac{100}{\%CO_{2d}} \\
 &= M_{NO_x} \frac{P_{std}}{R_u T_{std}} \frac{n_{NO_x}}{n_{exh}} (K_{cc}) 100 \frac{M_C}{M_C + \alpha M_H} \frac{n_{exh}}{n_{CO_2}} \\
 &= \frac{n_{NO_x}}{n_{CO_2}} \frac{M_{NO_x}}{M_C + \alpha M_H} \frac{P_{std} M_C}{R_u T_{std}} (K_{cc}) 100
 \end{aligned}$$

pt.16

For this to be equal to our fundamental formula for fuel specific NOx, the “magic number” K_{cc} would have to be given by

$$\begin{aligned}
 fsNO_x &= \frac{n_{NO_x}}{n_{CO_2}} \frac{M_{NO_x}}{M_C + \alpha M_H} \frac{P_{std} M_C}{R_u T_{std}} (K_{cc}) 100 = \frac{n_{NO_x}}{n_{CO_2}} \frac{M_{NO_x}}{M_C + \alpha M_H} \\
 \Rightarrow K_{cc} &= \frac{R_u T_{std}}{P_{std} M_C} 10^{-2}
 \end{aligned}$$

pt.17

We can do the calculation to check this theory against the value of 0.321 [(scf/lb)/%] specified in Method 19.

$$\begin{aligned}
 K_{cc} &= \frac{R_u T_{std}}{P_{std} M_C} 10^{-2} \\
 &= \frac{1545.3 [\text{ft lbf/lb mole exh/R}] \times (459.67 + 68) [\text{R}]}{29.92 [\text{inHg}] \times 12 [\text{lb C/lb mole C}]} \times \\
 &\quad \frac{10^{-2}}{144 [\text{in}^2/\text{ft}^2] \times 0.48977 [\text{lbf/in}^2/\text{inHg}]} \\
 &= 0.322 [\text{scf / lb C}]
 \end{aligned}$$

pt.18

So, we again have good agreement between our calculations and Method 19 constants. We therefore conclude that Method 19 is equivalent to the fundamental equation and we can write

$$f_s NO_x = C_{NO_x} (K_{cc} \%C) \frac{100}{\%CO_{2d}} = \frac{n_{NO_x}}{n_{CO_2}} \frac{M_{NO_x}}{M_C + \alpha M_H}$$

pt.19

Heating Value Specific Emissions

If we need to report the heating value specific emissions per Method 19

$$E = C_d \frac{K(K_{cc} \%C)}{GCV} \frac{100}{\%CO_{2d}}$$

pt.20

it is apparent that we will need to have the fuel analyzed to determine the gross calorific value.

If we are only concerned with total mass emissions, the calculated fuel specific emissions can be multiplied by the instantaneous fuel rate and the result can be integrated over time.

$$m_{X,tot} = \int_t \dot{m}_{fuel} f_s X dt$$

pt.21

If fuel specific emissions calculations disturb a regulator or confuse the standard CEMS software, a representative gross calorific value can be used. The total mass can then be calculated as the instantaneous fuel rate times the gross calorific value times the calculated heating value specific emissions all integrated over time.

$$m_{X,tot} = \frac{GCV}{K} \int_t \dot{m}_{fuel} E dt$$

pt.22