Consistent Emission Correction Factors Applicable to Novel Energy Carriers and Conversion Concepts

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Abstract

Volume correction factors have been an important aspect when reporting pollutant emissions from gaseous combustion for many years. Their application has become standard procedure in such a way that their applicability is seldom questioned. However, their emergence dates back to a time when power generation primarily relied on conventional fuels such as coal and gas. The advent of alternative fuels and new combustion concepts reveals the classical correction formula prescribed by current regulations to produce results that can be misleading when comparing different mixtures with regard to their emission behavior. For this reason, this work derives a more generalized correction formula that is applicable to arbitrary fuel-oxidizer combinations and is based on the same principles as conventional volume correction. The impact of the choice of correction formula is then illustrated by comparing results for various fuels for a simple equilibrium calculation as well as experimental data from a premixed swirl combustor and a pulse detonation combustor. The results show that the derived correction terms allow for an unbiased comparison of emission behavior in a similar manner as alternative fuel mass based metrics such as emission index, as long as the amount of intermediate reactants and radicals within the exhaust gas remains comparably low. It is suggested that future emission regulations should incorporate the issues discussed in this work to ensure unbiased comparison of emission values across a wide range of combustion applications.

Keywords: Pollutant emissions, Correction factors

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1. Introduction

With continuing efforts to decrease the share of fossil resources across all applications of combustion processes, an increasing diversification of combustion fuels can be observed. Renewed interest in hydrogen or ammonia based fuel blends as well as possible synthetic fuels enforces new approaches with regards to fuel flexibility. In addition, various oxy-fuel concepts which combine a combustible mixture of fuel and pure oxygen with recirculated flue gas strive to allow for carbon-free emissions by CO_2 sequestration.

In the context of gas turbine combustion, this new plethora of combustible mixtures is not yet truly recognized in regulations and practices concerning the control of pollutant emissions, although cases for adjusted standards have already been made [1]. The current limits for industrial-sized gas turbines in Europe are set by Directive 2010/75/EU of the European Council [2], which defines maximum gaseous pollutant emissions in the form of mg/Nm^3, with Nm^3 referring to the gas volume at standard conditions (273.15 K and 1 atm). Currently, it only defines a general limit of $50\,mg/Nm^3$ (with some alleviation if certain efficiency goals are met) for gas turbines operated with natural gas containing up to 20 % of other constituents and a limit of $120\,mg/Nm^3$ in case of other gases.

Adhering to this general framework, most scientific or industrial publications covering gaseous pollutants from stationary combustion devices choose to quantify them based on concentration measurements. In contrast, automotive emissions tend to be given in g/km and aerospace regulations require an emission index EI of the kind mg/kg_{fuel} or mg/MJ.

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Eventually, all these metrics aim to quantify the amount of harmful substances that are released by a specific combustion process. However, concentration based measurements in particular require special attention when it comes to effectively separate the emission behavior of a combustor from purely dilutional effects that might arise from the choice of operating conditions or the particular composition of the combustion fuel. The latter determines the amount of oxidizer required for complete combustion, which might introduce additional inert diluents to the mixture, e. g. nitrogen in case of air.

Thus, to allow for an unbiased comparison of various combustion systems, common practices and correction factors have been derived. Publishing unaltered volumetric pollutant measurements makes sense when assessing their impact on the immediate surroundings of the emission source. However, using them to quantify pollutant emissions from power generation or industrial processes on an atmospheric level can be ambiguous: air dilution resulting from lean combustion or additional bleed and process air reduces pollutant concentrations inside the exhaust gas without changing the overall amount of harmful substances that are released. For this reason, it has long been common to correct measured concentrations to a reference volume defined by a specific water and oxygen content. For instance, Directive 2010/75/EU defines its limits for stationary gas turbines based on an O_2 volume fraction of 15 % after correcting for the amount of water vapor within the exhaust gas.

This practice of emission correction has been applied for decades and thus became such a standardized procedure that the limits of its applicability have seldom been pointed out. Because despite its straightforwardness for conventional combustion processes which primarily rely on natural gas and the exhaust composition of which is only impacted by air dilution, it gets more complex for processes that employ varying O_2/N_2 ratios due to either oxygen enrichment or exhaust gas recirculation (EGR). The issue is e. g. addressed in the work by Burdet et al. [3], in which it is decided to rather publish uncorrected concentration measurements for the analyzed combustor due to the "artificial decrease" in NO_x emissions that EGR would cause. ElKady et al. [4] and Li et al. [5] discuss several ways of reporting NO_x emissions for the examined EGR combustor and eventually derive an adapted correction formula tailored to their needs. They acknowledge that EGR is mathematically beneficial for NO_x correction due to the decreased O_2 concentration in the exhaust gas, which is why they generally recommend to use mass-based emission metrics such as Emission Index. The same mathematical advantage of nitrogen addition is mentioned by York et al. [6]. Similarly to [4, 7], Weiland et al. [8, 9] developed their own correction formula for nitrogen-diluted hydrogen diffusion flames. Best et al. [10] examined emission behavior for CO_2-enriched combustion in a micro-gas turbine. Referring to the discussion by Ekady et al. [4], they chose to report NO_x emission levels in the form of an Emission index per net power output to avoid any bias resulting from EGR when using a concentration based metric.

Similar issues arise when fuel blends are considered, with the most practical contemporary example being H_2-enriched natural gas. A recent paper by Douglas et al. [11] addresses the issue by pointing out the dependence of the "classical" oxygen correction factor on the amount of hydrogen added to natural gas/methane. Additional correction factors to account for this bias are supplied. However, it must be pointed out that these corrections only deal with the influence of varying fuel composition on the oxygen and moisture correction terms. The accompanying changes in overall exhaust gas volume are only partly and indirectly incorporated by the additional assumption of a constant combustion temperature and molar fuel amount which further restricts the generality of this approach.

Thus, it appears that the established emission correction practices for concentration measurements, while still being widely applied in the combustion community, are in fact insufficient to capture all possible biases arising from a more diversified combustion landscape. This work thus aims to rectify these shortcomings by deriving a more generalized form of concentration correction factors that enables the comparison of gaseous pollutant emission measurements for arbitrary fuel-oxidizer combinations while remaining fully consistent with the already established methods. These suggestions could thus also serve as a basis for adjusted future emission regulations.

2. Volumetric correction factors

Volumetric correction of gaseous emission measurements has been a common practice at least since the advance of lean premixed gas turbine combustion. As formulated by S. R. Turns [12]: "The purpose of correcting to a specific O_2 level is to remove the effect of various degrees of dilution so that true comparisons of emission levels can be made, while still retaining a familiar mole-fraction-like variable."

Calculations involving gas volumes usually carry the additional complication that the volume taken by a specific amount of gas molecules is temperature and pressure dependent. For this reason, all references to volume in this work assume the volumes to be at identical pressure and temperature conditions. If additionally all gases are treated as ideal gases, as it is common in emission analysis, this also renders volume fractions and molar fractions to be equivalent.

Mathematically, volumetric correction for concentration measurements simply replaces the actual exhaust gas volume V with a reference volume V_ref with a known grade of dilution:

$$c_{i,\text{corr}} = \left(\frac{n_i}{V}\right)_\text{corr} = \left(\frac{n_i}{V}\right)_\text{meas} \frac{V}{V_\text{ref}}, \tag{1}$$

with species molar amount n_i. It is obvious that the thus corrected concentration only depends on the absolute amount of emitted species n_i and the reference volume V_ref. A decrease in the latter would increase oxygen corrected concentration levels, even if the actual amount of pollutant n_i remained the same.

Neither V nor V_ref need to be known explicitly because their ratio can be determined solely by knowing their respective primary species composition. An example is the well-established correction formula

$$\begin{aligned} c_i^\text{dry,ref} &= \frac{V}{V_\text{dry}} \frac{V_\text{dry}}{V_\text{dry,ref}} c_i \qquad (2) \\ &= \frac{1}{1 - X_{H_2O}} \frac{0.21 - X_{O_2}^\text{ref}}{0.21 - X_{O_2}} c_i, \qquad (3) \end{aligned}$$

which corrects the measured concentration value c_i in a potentially wet exhaust gas with a measured O_2 molar fraction of X_{O_2} to a reference exhaust volume devoid of any water and with a fixed O_2 molar fraction of $X_{O_2}^\text{ref}$. This correction separates dilutional effects due to varying equivalence ratios and added cooling air from their actual effect on reaction kinetics and thus allows for a fair comparison of combustion systems regardless of their use of air in the overall process. It has the advantage that only the water and oxygen content of the exhaust gas sample have to be measured sufficiently accurate while the complete composition does not have to be known. However, as pointed out in [13], a concentration based metric does not inherently "reward" more efficient processes, in contrast to emission indices which can also be decreased by increasing fuel efficiency.

The derivation of Eq. 3 also assumes that the diluent has a molar O_2 content of 21 %. This renders it invalid in cases of oxygen enriched combustion atmospheres, as was shown by Garg and Castaldini [14]. Starting from an idealized general combustion reaction of a fuel of which the principal constituents are C, H, O_2, Cl or other halogens, and S, the following formula for the dry exhaust volume is derived:

$$\begin{aligned} V_\text{dry} = (n_\text{C} + n_\text{S}) &\left(1 + \frac{n_\text{N2}}{n_{O_2}}\right) \\ &+ \frac{n_{N_2}}{n_{O_2}} \frac{1}{4} (n_\text{H} - n_\text{Cl}) \\ &+ n_{EO_2} \left(1 + \frac{n_\text{N2}}{n_{O_2}}\right) \\ &- \frac{n_{N_2}}{n_{O_2}} n_{O_2}^f \end{aligned} \tag{4}$$

Each n_s represents the amount of element or species s within each fuel molecule or within the oxidizer in case of n_{N_2} and n_{O_2}. n_{O2}^f represents the fuel bound oxygen, while n_{EO_2} refers to "excess" oxygen, that is, the measurable oxygen remaining in the exhaust gas after combustion has completed. Consequently, the first term is equal to the volume of the combustion products CO_2 and SO_2 as well as the amount of nitrogen accompanying the oxygen used in their formation. The second term corresponds to the nitrogen accompanying the oxygen that has already been removed in form of water vapor, corrected by the amount of hydrogen that could not form water because it was already used up by the formation of HCl. The third term constitutes the excess oxygen still present in the exhaust gas and the corresponding nitrogen, while the last term corrects this for the amount of fuel bound oxygen, or rather the fact that this oxygen does not bring any nitrogen with it.

Inserting Eq. 4 into Eq. 3 with some reformulations than lead to an adjusted general correction formula of

$$\frac{V_\text{dry}}{V_\text{dry,ref}} = \frac{0.21 - X_{O_2}^\text{ref}}{X_{O_2}^+ - X_{O_2}} \left(1 - \frac{X_{O_2}^+ - 0.21}{\alpha + 0.79}\right) \tag{5}$$

with $X^{+}_{O_2}$ as the O_2 mole fraction in the enriched oxidizer and

$$\alpha = \frac{n_C + n_S + n_{N_2}}{(n_H - n_{Cl})/4 - n_{O_2} - n_{N_2}}$$

as a fuel composition parameter. With no enrichment, Eq. 5 reduces to the simple term from Eq. 3. For hydrogen as fuel, $\alpha = 0$ and the corresponding equation has already been applied for oxygen correction of O_2 enriched mixtures in [15].

It is important to point out that $V_{dry,ref}$ in this case refers to the exhaust volume that the same molar amount of fuel would produce in combustion with *unenriched* air that would lead to an exhaust O_2 molar fraction of $X^{ref}_{O_2}$. In terms of Eq. 1, this means that $V_{dry,ref}$ remains the same regardless of the grade of enrichment, which allows $c_{i,corr}$ to be only changed by pollutant molar amount n_i. Because the relation of molar amount to mass is fixed for a particular species, concentration measurements corrected in this fashion once again become the de-facto mass emission metric they were intended to be. Naturally, Eq. 5 is also applicable in the presence of oxygen depletion, for example in the context of EGR.

But even when disregarding oxygen enrichment, Eq. 3 is unsuited for the comparison of emission levels of different fuels. This is because the size of the reference volume $V_{dry,ref}$ resulting from the assumed reference dry O_2 content is fuel-dependent. As shown in Fig. 1, these volumes can differ significantly and also depend on which additional assumptions about the combustion process are made. For instance, one mole of H_2 requires less air to fully combust than one mole of CH_4, decreasing the exhaust volume accordingly. As a result from Eq. 1, a combustion system that would produce the same amount of pollutant from burning H_2 as when using CH_4 would then still end up with a higher corrected concentration for H_2 due to the decrease in (reference) exhaust volume.

Thus, to maintain a separation between the effect of the specific fuel stoichiometry and the actual impact of the choice of fuel on pollutant formation, it seems reasonable to follow the example of Eq. 5 by correcting all concentration measurements to the same reference volume, regardless of which fuel was actually used. In doing so, the correction factor becomes

$$\frac{V_{dry}}{V_{dry,ref}} = \frac{0.21 - X^{ref}_{O_2}}{X^{+}_{O_2} - X_{O_2}} \left(\frac{\alpha + 1 - X^{+}_{O_2}}{\alpha^{ref} + 0.79} \right) \frac{\beta}{\beta^{ref}} \qquad (6)$$

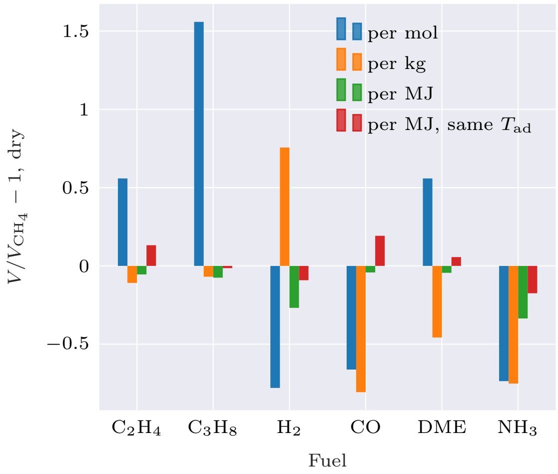


Figure 1: Reference volume for various fuels compared to CH_4. All fuels combusted in air, except for NH_3 using enriched air with 30 $\%_{vol}O_2$ to reach the same T_{ad}.

with

$$\beta = (n_H - n_{Cl})/4 - n_{O_2} - n_{N_2}$$

and α^{ref} and β^{ref} referring to their values for a common reference fuel, e. g. CH_4. Since this enhanced factor removes the impact of exhaust volume fluctuation displayed in Fig. 1, each of the blue columns directly corresponds to the error made when comparing the pollutant emissions made by various fuel if Eq. 3 is used instead of Eq 6.

However, while this new factor now allows for the comparison of pollutant emission for arbitrary fuels and with an arbitrary amount of oxygen enrichment (or depletion), it compares them on a molar basis. From a more practical point of view, a comparison based on fuel mass or power output is more desirable, as can be seen in the earlier definitions of the Emission Indices for automotive and aerospace combustion devices.

Figure 1 also displays the relative differences in $V_{dry,ref}$ when comparing the same mass (orange) or energy content (green) for different fuels. Additionally, the red columns display the relative exhaust volume for each fuel if the same amount of combustion energy is released and the adiabatic flame temperature is held constant by adjusting the equivalence ratio. In the case of NH_3, oxygen enrichment must be employed additionally to allow the adiabatic flame temperature to reach the same value as for the other fuels. For the same energy, the error made when ignoring the differences in exhaust volume reduces but can still reach up to 30 % depending on the fuel. It will also increase for higher

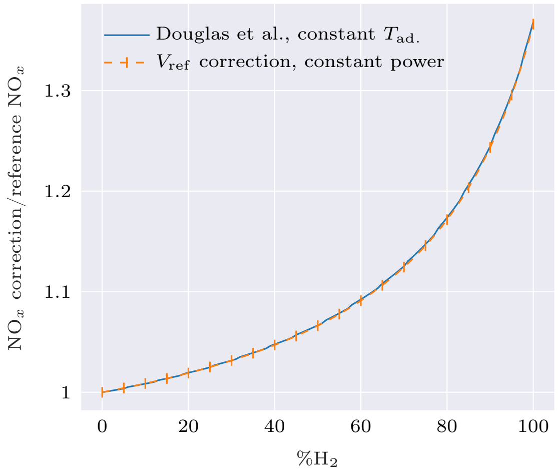


Figure 2: Relation of NO_x correction factors for varying CH_4-H_2 blends

levels of O_2 enrichment, because of the higher ratio of combustion products to inert gas within the exhaust volume.

To change Eq. 6 from a molar comparison to an energy-based comparison, the β parameter can be extended by the energy content of the corresponding fuel, for instance

$$\beta' = \frac{\beta}{\mathrm{LHV}} \tag{7}$$

with LHV being the lower heating value per volume of fuel. Whether the LHV is a suitable metric depends on the individual combustion conditions: Rich mixtures and/or very high flame temperatures can lead to a significant presence of intermediate or radical species in the exhaust gases that will retain some of the chemical energy that would be released in the case of complete combustion. In these cases, more appropriate power output figures that account for combustion and overall efficiency should be chosen instead. However, because the definition of α is based on the assumption of complete combustion, results should be considered with care as soon as a significant amount of intermediates remains present in the exhaust.

The energy adjusted formulation allows to compare the resulting NO_x correction factors when determined using Eq. 6 with those postulated using equilibrium chemistry calculations in [11] in Fig. 2. Near perfect agreement is found only when using the molar lower heating values to allow for an energy density weighted V_{ref} in accordance with Eq. 7. This might seem surprising because energy weighting is not made explicit in the data from [11]. It is, however, implicitly enforced by maintaining a constant adiabatic flame temperature for the same molar amount of fuel. An additional implicit requirement for the shown equivalence is that both the analyzed fuel and the reference fuel must have similar molar heat capacities. The subtle reliance on such implicit assumptions thus once more stresses the importance of correction factors that explicitly state the assumptions that lead to their derivation. Much confusion and unreliable comparisons can be the result otherwise, as will be shown again in the next section.

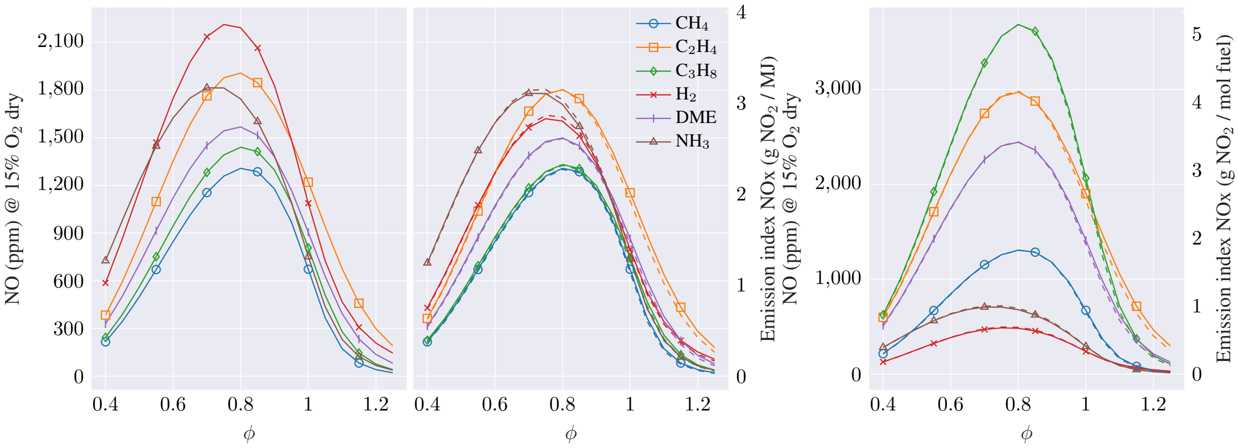
3. Significance for pollutant emission comparison

To demonstrate the significance of the choice of the oxygen correction factor when comparing the emission behavior for various fuels, emission behavior of various applications is analyzed for a variety of fuels. The first example are numerically determined NO_x equilibrium concentrations. The second example looks at experimental results from a permixed swirl burner capable of performing with natural gas as well as hydrogen. The last case compares measured NO_x emissions from a Pulse Detonation Chamber (PDC) for hydrogen and ethylene under oxygen-enriched conditions.

3.1. NO_x Equilibrium Concentrations

NO_x equilibrium concentrations for CH_4, C_2H_4, C_3H_8, H_2, DME and NH_3 are calculated and analyzed using the chemical equilibrium solver of the Cantera software package [16]. Thermodynamic and chemical kinetic data are delivered by the San Diego kinetic mechanism that includes multistep NO_x chemistry [17]. Although NO_x equilibrium values are seldom relevant in practical systems due to short combustor residence times, they can serve as a benchmark to compare dilutional effects and their suppression by the adjusted correction factors.

Figure 3a shows NO_x equilibrium concentrations corrected according to Eq. 5. That means that O_2 enrichment, as it is present for the NH_3 mixture to counter its limited reactivity, is taken into account. Nevertheless, values for each fuel are corrected to the reference volume specific to that fuel, which can vary significantly as was shown in Fig. 1. From this comparison, one would conclude that CH_4 and H_2 are the best and worst choices, respectively, with



(a) Individual V_{ref}

(b) $V_{\mathrm{ref}}^{\mathrm{CH4}}$, energy weighted

(c) $V_{\mathrm{ref}}^{\mathrm{CH4}}$, mole weighted

Figure 3: Equilibrium $\mathrm{NO_x}$ concentrations for various fuel-air (NH_3 with $30\,\%O_2$-$70\,\%N_2$) mixtures at $T_0 = 300\,\mathrm{K}$ and $p_0 = 1\,\mathrm{bar}$, corrected to $15\,\%O_2$ dry reference volume using different reference volumes and weightings. Dashed lines in Figs. 3b and 3c represent emission index.

regard to their $\mathrm{NO_x}$ emission levels, with C_2H_4 and NH_3 residing in between with comparable results and C_3H_8 and DME closer to methane. The shift of the NH_3 curve towards leaner mixtures is a direct result of the O_2 enrichment.

When instead looking at Fig. 3c, which uses Eq. 6 to correct all concentrations to a common reference volume (that of CH_4), a different result can be found: Here, the increased volumetric energy density of the higher hydrocarbons results in high emissions per molar amount of fuel, while for the same reason benefiting H_2 and NH_3. Looking back at Fig. 1 and Fig. 3a proves that this trend is masked if the significant increase in the higher hydrocarbons' individual reference volume is not accounted for.

Also displayed in Fig. 3c is the molar $\mathrm{NO_x}$ emission index

$$\mathrm{EI}_{\mathrm{mol}} = c_{\mathrm{NO}} \frac{M_{\mathrm{NO_2}}}{\bar{M}_{\mathrm{exh}}} \frac{M_{\mathrm{fuel}}}{Y_{\mathrm{fuel}}} \tag{8}$$

with $M_{\mathrm{NO_2}}$, $\bar{M}_{\mathrm{exh}}$, and M_{fuel} as the molar masses of NO_2, the overall exhaust gas, and the fuel, respectively, and Y_{fuel} as the fuel mass fraction within the reactants. It can be seen that EI_m agrees qualitatively very well with concentration data corrected using Eq. 6, with mostly only a constant scaling factor separating the two. Rearranging Eq. 8, this factor can be found to correspond to $M_{\mathrm{NO_2}} V_{\mathrm{ref}} / V_{\mathrm{fuel}} \cdot 10^{-3}$, which is a constant for a common reference volume and molar/volumetric fuel amount. Differences grow more pronounced for richer mixtures, because the volumetric correction terms assume complete ideal combustion and do not account for the increasing amount of intermediates present in the exhaust gas under these conditions. We can thus conclude that correcting pollutant concentrations to a common reference volume produces data that is *equivalent* to an emission index with regards to the relative emission levels of each fuel, at least for fuel-lean conditions.

While emission indices are conceptually easier to grasp, calculating them based on Eq. 8 brings two challenges: since they depend on $\bar{M}_{\mathrm{exh}}$, full knowledge (or at least sufficiently accurate assumptions) of the full composition of the wet exhaust gas is required. However, the above listed correction factors are also based on idealized combustion species balances, so errors potentially arising from inaccurate assumptions might be shared by both methods. With that being said, correction terms based on the assumption of complete combustion will become less accurate for fuel rich mixtures, because the increased presence of fuel intermediates distorts the volume ratio between actual combustion products and reference volume. In this case full knowledge of the exhaust composition is required and mass based metrics such as emission index can be more useful. However, their reliance on mass conservation requires all concentration measurements that are to be turned into emession indices to be taken on a wet basis. While this might be feasible for in situ measurements, extracting samples without condensation becomes challenging especially for fuels that produce exhaust gas of high moisture like H_2 or NH_3. Alternatively to Eq. 8, emission indices could also be derived by determining the total exhaust volume flow, either wet or dry depending on the corresponding emission measurement. But even though this could circumvent the problems related to wet concentration measurements by using dry gas samples, determining the corresponding total dry exhaust volume flow would either once more require precise measurements of water vapor and careful avoidance of any condensation, or the direct measurement of the dry exhaust volume flow by the extraction of the entire water content.

As discussed before, comparing fuels based on their molar or mass amount is often of limited value in practical considerations. A comparison based on their respective energy output is therefore more enlightening. For this reason, Fig. 3b displays corrected concentration data that made use of the extended β parameter to additionally weigh all data with their respective fuel's LHV. The same is done with the molar emission index, once again reaching excellent qualitative agreement.

In this metric, both alkanes show very similar NO_x emission characteristics and perform best, but overall relative differences between fuels are reduced compared to the data of Fig. 3a without the adjusted correction factors. This especially benefits hydrogen, which shows the most dramatic change compared to the correction according to Eq. 5 in Fig. 3a.

3.2. Premixed Swirl Burner

Stationary combustion tests were conducted in an atmospheric test rig using a swirl-stabilized burner. A preheated air flow is guided through a radial swirler and subsequently undergoes vortex breakdown in a cylindrical combustion chamber made from quartz glass. A constant airflow was applied for all measurements to preserve the general structure of the flow field.

Natural gas from the grid (~97 vol% methane) and hydrogen from bottles (purity 99.9 %) were used as fuels. The fuel was injected at ambient temperatures directly into the combustion chamber, where the flame mainly stabilized in the shear layer of the central and corner recirculation zone.

Directly after the combustion chamber, exhaust gas was extracted with a suction pipe. The sample gas was dried and continuously analyzed for emissions. Nitric oxides measurement was based on chemiluminescence, and oxygen on its paramagnetic characteristic.

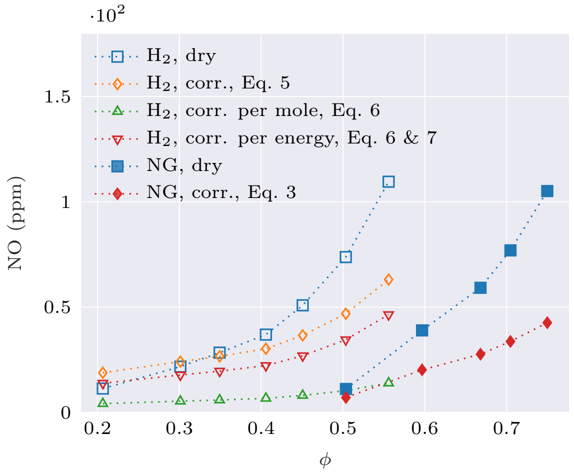


Figure 4: Comparison of measured and corrected NO_x emissions for premixed swirl burner with natural gas-air and hydrogen-air mixtures for constant air mass flow. Since CH_4 is chosen as the reference fuel, all correction values, that is Eqs. 3–6, are equivalent for NG.

Comparison of measured NO_x emission concentrations for a premixed swirls burner operated with natural gas and hydrogen at various equivalence ratios is presented in Fig. 4. All concentration measurements have been normalized to the maximum values measured for natural gas at the highest equivalence ratio. Air mass flow rate is kept constant. Naturally, correction terms for natural gas remain the same when it is chosen as reference fuel.

Emission characteristics display a significant shift in equivalence ratio that is tied to the higher adiabatic flame temperature of hydrogen for the same equivalence ratio which in turn causes higher thermal NO formation. While this trend remains unchanged after correction, oxygen correction of H_2 emissions without accounting for the change in reference volume results in the 37 % increase already reported in [11] when compared for the same energy release and more than four times as when compared per mole of fuel/fuel volume. The latter curve shows a relatively smooth transition between values for H_2 and NG because the effect of the vastly different stoichiometric air-fuel ratio is canceled out and the NO formation as per mole of fuel is relatively similar.

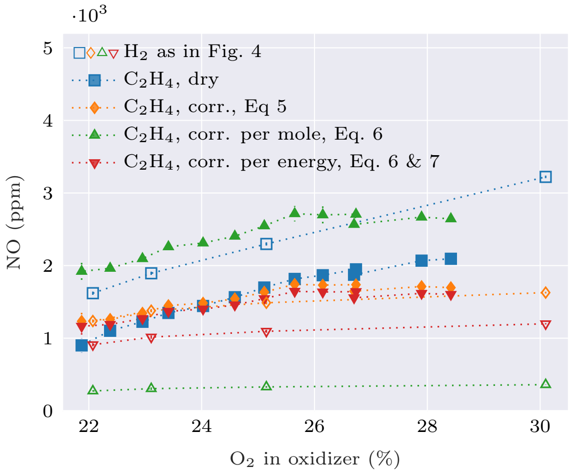


Figure 5: Comparison of measured and corrected NO_x emissions for pulse detonation combustion with H_2 and C_2H_4. Stoichiometric mixtures are maintained while oxidizer mass flow rate is kept constant.

3.3. Pulse Detonation Combustion

NO emission measurements for a pulse detonation combustor (PDC) are shown in Fig. 5. The principle of PDC is based on the cyclic operation of a cylindrical combustion chamber in which a strongly supersonic shock wave propagates through a reactive mixture and is thus driven by the chemical energy of the rapid ignition it instigates. Because detonation-driven combustion is thermodynamically very similar to a constant volume combustion, significant efficiency gains compared to conventional isobaric combustion are targeted and research interest remains high.

The current PDC test rig is described in detail in [18] and is operated with either H_2 or C_2H_4. While a constant oxidizer mass flow is maintained, oxidizer composition is varied by enriching air with additional oxygen. The impact of the amount of enrichment on NO_x emissions is studied. To ensure reliable deflagration to detonation transition (DDT) within the limited dimensions of the test rig's combustion chamber, it was found that enrichment to at least 22.5 % O_2 in the oxidizer was necessary. The fuel mass flow rate is adjusted for each operational point to ensure stoichiometric mixtures throughout the analyzed composition range. Operating frequency is 5 Hz for C_2H_4 and 10 Hz for H_2. The reported values can be viewed as cycle-average emissions because of the unsteady cyclic nature of PDC operation.

As has been shown in previous works on the topic [15, 19], NO_x emissions from PDC devices can be quite significant when operated under near-stoichiometric and/or oxygen enriched conditions and in this case can reach up to several thousand ppm. Since the error introduced by the correction factor that is discussed here is always relative to the measured values, its absolute range grows accordingly.

Because of the difference in operating frequency, direct comparison of measured dry emission values for both fuels has little significance: half the frequency equals to roughly double the amount of air dilution. For this reason, oxygen correction of pollutant concentration measurements is especially important for cyclic combustion systems such as PDC. Applying the conventional correction formula from Eq. 3 shows both fuels to have very similar emission behavior. However, when taking changes in reference volume into account by using Eq. 6 with methane once more as the reference fuel, the impact of the vastly different fuel stoichiometry becomes visible: when compared per mole (or m^3) of fuel, ethylene emits five times as much NO as hydrogen. These differences are much more moderate when taking the difference in energy density into account, but NO levels of C_2H_4 remain 25 %-33 % above those of H_2 for the same O_2 enrichment level.

4. Conclusion

It was found that the choice of the oxygen correction factor has significant impact on the absolute and relative emission levels when reported on a concentration basis. While some efforts have already been made in the literature to adjust classical correction formulas to specific conditions of fuel blends or varying oxidizer composition, these attempts focus only on specific application cases and do not provide a general solution that allows for sensible correction factors for arbitrary fuel and oxidizer mixtures.

Since the original intention when introducing oxygen correction to gaseous pollutant measurements was the desire for a common reference volume that would discard all influence of possible dilution, inter-fuel comparisons require a common reference volume defined for a single reference fuel to account for the effect of fuel-specific stoichiometry. It was shown that correction factors created according to this produce data that effectively equal an emission index similar the ones already in use for aerospace and automotive regulations.

One marked disadvantage of these heavily corrected concentration values is their loss of physical significance. While measured concentrations represent a physical ability, that is, the amount of molecules in a sample volume, corrected concentrations merely represent a metric of comparison. However, this could be argued for oxygen corrected values in general.

While emission indices provide an alternative metric of which the physical meaning is relatively straightforward, their reliance on mass balancing requires an accurate assessment of the moisture of the exhaust gas which can be challenging in many application scenarios that involve very moist combustion products. Thus, in many cases, relying on concentration-based measurements can be significantly more convenient.

In conclusion, when comparing different fuels regarding their pollutant emissions, the metric to do so should match the overall goal of the comparison: measured emission levels should be analyzed unaltered to reflect the actual physical pollutant concentrations in the direct vicinity of the exhaust and thus assess the immediate health risk they pose. However, if overall atmospheric contribution is to be considered, oxygen correction is indicated. Here, correction to a common reference volume or calculation of an emission index are necessary to allow for sensible comparison, with energy weighed values delivering the most practical value.

Finally it should be stressed once more that publishing emission values in terms of corrected concentration values without proper acknowledgment for fuel or oxidizer composition can lead to results that are ambiguous at best and misleading at worst. Consequently, these issues should also motivate attempts to reformulate current emission limit regulations. To better capture the recent development in fuel-oxidizer diversification and facilitate comparison of combustion systems across all technological concepts, metrics such as Emission Index or the concentration factors provided in this work should be employed instead of the current approach that is only targeted at excess air correction.

Acknowledgments

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