NO_x Emissions from Hydrogen-Methane Fuel Blends

Christopher Douglas, Research Engineer, Georgia Institute of Technology

Benjamin Emerson, Senior Research Engineer - Georgia Institute of Technology

Timothy Lieuwen, Executive Director - Strategic Energy Institute, Georgia Institute of Technology

Tom Martz, Principal Technical Leader - Electric Power Research Institute

Robert Steele, Technical Executive - Electric Power Research Institute

Bobby Noble, Gas Turbine Programs Manager - Electric Power Research Institute

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Concerns associated with climate change are leading to a variety of new proposals to reduce the carbon dioxide (CO_2) emitted by global energy and transport systems. In addition to producing CO_2 , many energy systems also release a variety of pollutants to the atmosphere, raising environmental and respiratory health concerns. As such, emissions associated with the combustion of fuels are regulated by a variety of national and local authorities. For example, in the US, subpart KKKK of the EPA code lays out federal emissions limits for nitrogen oxides (NO_x) and sulfur dioxide (SO_2). The primary source of NO_x in most gas-fired systems comes from the ambient air itself, as its dominant constituents (nitrogen, N_2 , and oxygen, O_2) react together under high temperature conditions. A variety of proposals are in place to utilize hydrogen (H_2) as a green energy carrier which can be transported in pipelines and burned by a variety of stationary and mobile sources, such as power plants, heaters, and trucks. As a carbon-free fuel, hydrogen has the desirable property that its combustion releases no CO_2 . However, H_2 combustion does generate NO_x since, as noted above, NO_x is formed when air is heated to high temperatures.

From a NO_x emissions perspective, the combustion of fuel blends containing H_2 raises two key issues. First, changes in fuel composition affect NO_x production pathways and, therefore, can directly alter the amount of NO_x generated by a system operating at a given power output. This issue is not addressed here, but is discussed in a companion white paper. Second, regardless of the actual NO_x emissions per unit of power, changes in fuel composition can indirectly influence the reported NO_x emissions due to details of the accounting and bookkeeping methods used to measure and report NO_x emissions across a variety of fuel blends and devices. This whitepaper focuses on the latter issue and, in particular, shows that many studies could be interpreting their NO_x emissions incorrectly by as much as 40% against high-hydrogen systems.

The environmental and air quality community has well-developed approaches to account for these variations which are factored into allowed emissions associated with air quality permits. Typically, these permitted levels can ultimately be traced back to net mass production of regulated pollutants. However, it is volumetric stack concentrations of pollutants, and not their actual mass production rates, which are actually measured using the continuous NO_x analyzers at the plant. As such, methods are needed to convert volumetric measurements (ppmv) to a mass basis (lb/MMBtu or lb/hr). For example, codes for gas turbine emissions often define allowable fractions of exhausted NO_x based on standardized sample preparation processes. In this standard process, the combustion products are sampled, the water is removed, and the dry sample is mathematically corrected simulate air dilution to 15% O₂ (for gas turbines) before measuring the NO_x levels. This correction approach is performed in order to evenly evaluate systems with varying levels of excess air. In the United States, typical stack exit permits are on the order of 3-30 ppmv @ 15% O2. However, the constant of proportionality between mass production of pollutants and this measured ppmv value is in fact fuel dependent. Again, this point is well known in the environmental community, and corrected via an "F-factor." However, a key motivator for this whitepaper is that the combustion community, which is currently evaluating low NO_x combustion technologies with results that are being used by a wide variety of stakeholders in evaluating the benefits of a hydrogen economy, is often not applying this correction and improperly comparing measured NO_x ppmv emissions between one fuel and another. For example, many papers in the literature are directly comparing NO_x emissions from methane/hydrogen blends, based on these NO_x ppmv concentration values. While this correction is negligible for many fuels (e.g., when comparing between natural gas and diesel fuel), it is very substantial for hydrogen.

However, as will be discussed in this whitepaper, at conditions with equal power output, hydrogen/methane fuel blends yield combustion products with higher proportions of H_2O and O_2 than pure methane. Hence, even when the mass production rate of NO_x emissions are identical, higher hydrogen systems will have higher composition-based value when reported in ppmv @ 15% O_2 . The next section presents a simple way to correct for this.



NO_x Corrections for H₂-containing Fuel Blends

To demonstrate the effect of fuel composition on NO_x emissions calculated using the dry concentration corrected to 15% O_2 , this section presents correction curves, assuming that the different blends are operated at the same flame temperature. Equilibrium chemistry calculations are performed for fuel blends ranging in composition from pure methane to pure hydrogen at constant adiabatic flame temperature. Assuming equal molar NO_x production across these conditions, the dry NO_x @ 15% O_2 , relative to that for pure natural gas are shown Figure 1. When using ppmv-based values, the emissions should be divided by the value on the vertical axis for a given hydrogen fraction. While the results in this plot are specific to the pressure and the reactant and flame temperatures noted in the caption, the correction curve varies only weakly for other conditions.

The key point is to show how a volume-based (ppmv) measurement approach can indicate higher NO_x emissions from H_2 -blended systems for the exact same mass of NO_x as a methane-fired plant. For example, this correction is about 7% for a 50%/50% H_2 /CH₄ blend, 17% for an 80%/20% blend, and 37% at 100% H_2 .

Although not shown, similar corrections for other common fuels are generally negligible. For example, consider the case of *n*-dodecane (an approximate simulation of diesel fuel), where the corresponding ratio between 100% methane and dodecane fuel for the two conditions shown in the appendix are 0.996 and 0.979, i.e., only 2%. This appears to be the reason that this correction is not widely appreciated in the combustion test community.

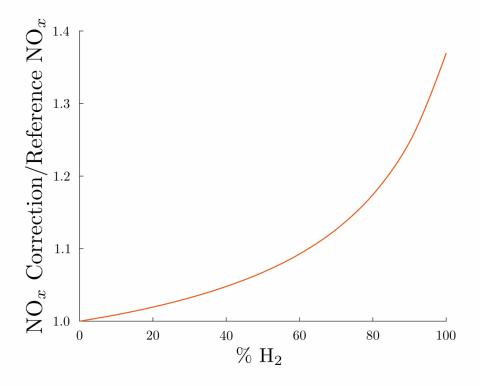


Figure 1: Dry NO_x emissions (in ppmv @ 15% O_2) for a constant temperature system operated at various hydrogen/methane ratios relative to the dry NO_x emissions from pure methane. When using ppmv-based values, the emissions should be divided by the value on the vertical axis for a given H_2 -fraction. Results calculated for 300 K reactants at 1 bar with adiabatic flame temperature of 2000 K.



Appendix: Tabulated Corrections

1 bar, 300 K reactants, Tad = 2000 K

Fuel % H ₂	Fuel % CH₄	Prod. %CO ₂	Prod. %H₂O	Prod. %O ₂	NO _x corr.	Ratio
0	100	7.69	15.38	3.70	0.4264	1.000
20	80	7.15	16.07	3.82	0.4347	1.019
40	60	6.39	17.03	4.00	0.4468	1.048
60	40	5.27	18.45	4.25	0.4659	1.092
80	20	3.46	20.74	4.66	0.5008	1.174
100	0	0.00	25.13	5.45	0.5840	1.370

20 bar, 700 K reactants, Tad = 2000 K

Fuel % H ₂	Fuel % CH₄	Prod. %CO ₂	Prod. %H₂O	Prod. %O ₂	NO _x corr.	Ratio
0	100	6.04	12.05	7.39	0.5414	1.000
50	50	4.61	13.78	7.76	0.5800	1.071
100	0	0.00	19.37	8.96	0.7528	1.390

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