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Pollutant Emissions Reporting and Performance Considerations for Hydrogen–Hydrocarbon Fuels in Gas Turbines

Hydrogen (H₂) fuel for gas turbines is a promising approach for long duration storage and dispatchable utilization of intermittent renewable power. A major global discussion point, however, is the potential air quality impact of hydrogen combustion associated with nitrogen oxide (NO_x) emissions. Indeed, several studies in the combustion literature have reported elevated NO_x concentrations in terms of dry ppmv NO_x at 15% oxygen (O₂) as a fuel's H₂ fraction is increased. Yet, as emphasized in this work, this practice of directly comparing emissions based on dry ppmv at a reference O₂ concentration (ppmvdr) is inappropriate across hydrogen and hydrocarbon fuel blends due to differing concentration changes induced by drying and referencing the corresponding exhaust gases. This paper addresses three distinct approaches for comparing emissions consistently across fuel blends. Furthermore, it presents examples that quantify the differences in the apparent pollutant emissions between each approach and the usual ppmvdr reporting practice across the full range of hydrogen–methane mixture ratios. In all of the considered approaches, ppmvdr emissions values are shown to be inflated for H₂ fuel blends relative to hydrocarbon fuels, making them unsuitable for direct comparisons of emissions among conventional and alternative fuels. [DOI: 10.1115/1.4054949]

1 Introduction

1.1 Background and Motivation. As the ramifications of global climate change continue to develop, so too does concern toward reducing carbon dioxide (CO₂) and methane (CH₄) emissions. Even so, the majority of the current global energy system is based upon fossil fuel combustion. Gas turbines in particular are a dominant global energy conversion approach due to their high efficiencies and low capital costs. Recently, a variety of proposals have been advanced to leverage hydrogen (H₂) as a carbon-free green energy carrier, whose energy can be utilized from a gas turbine on a dispatchable basis. Hydrogen can be readily generated with excess renewable power, transported in pipelines, stored, and burned in a variety of applications when and where it is needed. Yet, despite its clear advantages concerning greenhouse gas emissions, sustainability, and energy security, a variety of challenges

remain to be solved before any widespread incorporation of high %H₂ fuels into existing gas turbine infrastructure is feasible.

One such challenge, which is the main focus of this study, is the problem of nitrogen oxide (NO_x) emissions. NO_x is a regulated pollutant due to its link to respiratory health problems, smog, and acid rain. Yet, unlike CO₂, carbon monoxide (CO), particulates (e.g., soot), and sulfur oxides (SO_x), which all form from atoms within traditional fuels that are not present in H₂, the primary source of NO_x in most gas-fired systems is simply atmospheric air, whose dominant constituents, nitrogen (N₂) and oxygen (O₂), react spontaneously at high temperatures. Hence, NO_x emissions, already a major design obstacle in natural gas systems, will continue to be a challenge within the paradigm of H₂ fuels.

Another concern, which is not a focus of this study but should briefly be mentioned, is the challenge associated with high %H₂ fuels in lean, premixed combustion systems. Modern dry low NO_x combustors operate in the lean premixed regime, where the flame temperature can be controlled to minimize NO_x production, and where flames are stabilized by a balance between flame propagation and flow velocity. However, H₂ flames behave very

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Manuscript received June 23, 2022; final manuscript received June 25, 2022; published online July 28, 2022. Editor: Jerzy T. Sawicki.

differently from CH₄ flames, with up to 10× higher flame speeds at a given equivalence ratio, plus extreme sensitivity to flame stretch and thermal-diffusive instability. Such effects cause H₂-fueled systems to be more prone to flame flashback than their natural gas counterparts. They also shift parameter regions where combustion instability occurs [1,2], meaning that operational experience developed for natural gas systems must be adjusted for fuels containing H₂. Such issues are the focus of significant research and burner development programs.

Returning to the main emphasis of this study, the NO_x emissions from the combustion of high %H₂ fuel blends raise two key issues. First, fuel composition changes can directly alter the chemical pathways that produce NO_x. Thus, at a given power output, a system firing natural gas may emit a different amount of NO_x than an equivalent system burning fuels containing H₂. This issue is the topic of several investigations [3,4], including a companion paper [5]. Second, regardless of the true emissions, changes in fuel composition indirectly influence the reported emissions based on how the results are formulated [6]. Indeed, emissions can be reported on a concentration basis or as a normalized production rate (e.g., mass emitted per unit of energy). They can also be compared using a variety of different, but justifiably relevant, reference conditions such as flame temperature, equivalence ratio, thermal energy input, or useful work output. Such normalized quantities are useful for understanding the emissions characteristics of a given fuel across a range of devices and operating conditions. Crucially, however, each also influences the value of the reported pollutant emissions differently depending on the composition of the fuel. Quantifying such differences is not a difficult task, but the importance of doing so does not seem to be widely appreciated by the combustion community, which has traditionally focused on relatively standardized fuels with minimal variability. In fact, the main inspiration for this paper came from our observation that the combustion community largely uses a particular volumetric approach for quantifying and reporting emissions. This approach will be shown to be ill-suited for comparisons across different hydrogen–hydrocarbon fuel blends. Similar concerns are also likely to extend to other fuel blends involving non-traditional alternatives such as ammonia (NH₃) and alcohol. This paper is primarily directed toward the combustion research community to help inspire standard pollutant emissions reporting techniques that allow for fair emissions comparisons among conventional and alternative fuels.

1.2 Technical Overview. It should be pointed out that approaches to account for pollutant emission rate sensitivities to fuel composition have already been standardized by the environmental community. Such considerations are typically factored into emissions permits based on the net mass production of regulated pollutants relative to the useful shaft work output; e.g., as ng/J [7]. However, since the continuous gas analyzers used to monitor plants measure volumetric stack concentrations rather than mass production rates, a conversion is required to transform these volumetric measurements (e.g., ppmv) to a mass basis (e.g., kg/kWh or kg/hr). To facilitate this, the same emissions codes that limit the allowable mass of exhausted pollutants generally also define volumetric emissions standards along with a specified sample preparation process. In gas turbines, this process consists of two steps that occur between the sampling of the combustion products and the reporting of the measured pollutant emissions. The first of these steps is often a practical requirement, as wet gas interferes with the operation of many chemiluminescence-based gas analyzers used to measure pollutants. Here, the water is removed, and the dried sample's exhaust gas composition is physically measured in terms of dry ppmv (ppmvd) values. Next, the dried sample is postprocessed with a simulated air dilution step to adjust the measured O₂ concentration to a reference condition (typically 15% O₂). This second step is not practically necessary but is instead imposed by regulators in the gas turbine

industry to offset the strong dependencies of the measured pollutant concentration on a system's equivalence and bypass air ratios. Hence, the actual regulated quantity resulting from these two steps is an O₂-referenced dry ppmv value, which will be referred to as ppmvdr in this paper. Crucially, however, this sample preparation process also imbues the relationship between the pollutant mass production rate and the reported ppmvdr value with a fuel-dependent constant of proportionality.

To better explain this important point, consider the difference between the combustion process of a hydrocarbon and hydrogen. Making a molecule of water (H₂O) releases heat and only uses one oxygen atom. Making a molecule of CO₂ releases less heat and uses two oxygen atoms. Since hydrocarbon combustion requires more oxygen to make CO₂, ppmvdr values decrease from a correction factor that adds back the consumed O₂ and dilutes the mixture. Conversely, H₂ exhaust requires less dilution to reach a target O₂ concentration at the same operating point due to its lower O₂ consumption, giving it a smaller correction to reported ppmvdr values. Additionally, the drying process that removes H₂O from the exhaust gas concentrates the pollutant in hydrogen exhaust streams more than in hydrocarbon exhaust where H₂O is less prevalent. It should be emphasized that these differences are entirely artificial in the sense that they are explicitly introduced by the sample preparation process rather than by any real increase in pollutant production rates. In fact, this work will demonstrate that, under three distinct measures of “equal” emissions, the relative differences between the ppmvdr pollutant values of hydrogen and hydrocarbon fuels may be as high as 40% in favor of hydrocarbons due to the above effects. This indicates a clear misunderstanding within the combustion literature, as several studies have interpreted their emissions using quantitative comparisons of ppmvdr values across hydrogen–hydrocarbon fuel blends. Such results inevitably overemphasize the true pollutant emissions of high %H₂ fuels in comparison to strictly hydrocarbon fuels.

Within the environmental community, a fuel-dependent “F-factor” has already been developed to account for the influences of fuel composition on volumetric emissions reports [8]. However, these approaches are not widely utilized within the combustion community, resulting in the aforementioned instances of improper comparisons of pollutant emissions between one fuel and another based on ppmvdr values. This naivety is understandable, as reporting with regards to the common ppmvdr emissions standards seems logical in a laboratory or simulated combustor setting where the shaft work used by alternative mass-per-energy emissions regulations is not available. Furthermore, this has not been an important issue historically, as the ratio of hydrogen to carbon atoms does not vary so significantly across hydrocarbon fuels (e.g., between natural gas, propane, and even diesel), resulting in only minor changes to the exhaust gas composition and making the effects on ppmvdr values described above insignificant (as will be demonstrated in the results). This is a crucial distinction today, however, as the field evaluates low-NO_x H₂ combustion technologies that will have major impacts on the potential future H₂ economy. Our study will present methods that may be used by the combustion community to evenhandedly evaluate and compare pollutant emissions, including NO_x, across a large variety of fuel compositions.

Aside from the issue of pollutant emissions, the difference in composition of the exhaust gases between hydrocarbon and hydrogen flames also has some implications for the performance and operation of H₂-fired gas turbines. The most important of these differences is the higher water content in the exhaust of high %H₂ fuel mixtures. This trait leads to a higher exhaust gas specific heat relative to hydrocarbon flames (which have less H₂O and more CO₂), directly impacting the gas turbine output. Since electric power gas turbines are typically fired to a maximum rated turbine inlet temperature, the additional enthalpy held by exhaust gases from higher %H₂ fuels results in greater output at a given turbine inlet temperature. The higher exhaust gas specific heat also changes the balance of compressor power required per unit of

work extracted. Consequently, the Brayton cycle has better thermal efficiency (lower heat rate) for higher %H₂ fuel blends at a given turbine inlet temperature. However, in addition to these thermal efficiency gains, high H₂ content also influences gas turbines' maximum rated power output. In general, the peak temperature in a gas turbine (and, therefore, its maximum cycle efficiency) is limited by thermal loading constraints on the turbine blades. Compared to hydrocarbon flames, the higher proportion of H₂O in the combustion products of H₂ flames increases the thermal conductivity of the exhaust gases and enhances heat transfer to hot section components. This may necessitate a derating of the maximum turbine inlet temperature in some applications and may counteract the performance benefits of the higher exhaust gas specific heat [9].

The principal purpose of this paper is to highlight within the combustion community important issues associated with emissions reporting in the context of hydrogen–hydrocarbon fuel blends. In it, we will discuss and demonstrate three different potential methods for consistently comparing pollutant emissions across varying fuel compositions. First, we quantify the basic effect of the concentration-based dry, O₂-corrected emissions reporting standards by contrasting the effect of the sample preparation process across the spectrum of H₂ and hydrocarbon fuels at a constant flame temperature in Sec. 2.1. These results are shown to form an explicit relationship between ppmvdr and ppmv values across fuel blends under conditions of constant adiabatic flame temperature and equal true pollutant concentrations in the untreated exhaust gas in Sec. 2.2.1. In regards to NO_x emissions, this constant temperature and constant ppmv comparison are natural from a combustion fundamentals perspective, given the strong temperature sensitivity of NO_x formation rates. However, it does not account for the slightly different amounts of heat release required to achieve the same temperature as fuel composition changes. This leads intuitively to the second approach in Sec. 2.2.2, where the emissions rate is quantified in terms of the emitted mass per unit of heat release. Here, we also evaluate the fuel-specific relationship between the apparent emissions determined from a mass-per-heat approach and the standard ppmvdr method. The mass-per-heat metric accounts for a broader range of thermodynamic effects associated with the properties of the combustion byproducts while remaining independent of the cycle. Therefore, in Sec. 2.2.3, the emissions rate is quantified in terms of a third approach: the emitted mass per unit of useful shaft work, which is a common method for regulating emissions in gas turbines. This ratio is not only a function of thermodynamic properties but also of cycle efficiencies, which are affected by fuel composition through such effects as differences in the specific heat ratios, among others. We then provide results for an example F-class gas turbine cycle and compare the ppmvdr emissions values that result in equal pollutant mass-per-work conditions across fuel blends. In all examples, as summarized in Sec. 2.3, our results show that ppmvdr emissions values are significantly inflated for high %H₂ fuels relative to hydrocarbons, making them improper for direct comparisons of emissions in the context of H₂-blended fuels.

2 Results and Discussion

As explained in the Introduction, the sample preparation procedure associated with ppmvdr-based emissions comparisons inflates the apparent emissions values in high %H₂ fuel blends relative to hydrocarbon fuels. A concrete and detailed demonstration of this process is given below. Then, three alternative approaches for comparing emissions across fuel blends in a consistent manner are evaluated, while considering procedural and technical details of the implementation associated with each. As part of this evaluation, sample calculations are used to quantitatively compare pollutant emissions reported using each metric with the common ppmvdr reporting approach for the complete range of H₂–CH₄ blends.

The examples in this section are based on equilibrium chemistry calculations performed using ANSYS CHEMKIN for fuel blends ranging in composition from 100% methane to 100% hydrogen reacting with air at a constant adiabatic flame temperature of $T_{ad} = 1800$ K. This constant temperature comparison is especially important for interpretations directed toward NO_x emissions, given the strong temperature sensitivity of NO_x formation rates. We separately consider two cases, designated as “atmospheric” combustion (1 atm and 300 K reactants) and “compressed” combustion (17 atm and 700 K reactants). Tabulated results of the major combustion products (excluding N₂) from the chemical equilibrium calculations of each case are reported in Table 1. In addition to the hydrogen–methane blend data shown in Table 1, we have also performed identical calculations for n-dodecane (C₁₂H₂₆, an approximation of diesel/jet fuel) and propane (C₃H₈) in order to generalize our results to a wider range of hydrocarbon fuels.

2.1 Demonstration of Fuel Composition Impacts on Reports of Volumetric Dry Emissions at 15% O₂. Using the volumetric concentrations shown in Table 1, we now proceed to explicitly demonstrate the dry, O₂-referenced emissions reporting procedure, which is standard in gas turbines. As explained in Sec. 1.2, this procedure consists of two steps between the collection of the sample and the reporting of the measurement. In the first step, all of the H₂O is removed from the sample. This results in a drying factor given as

$$A_1 = \frac{1}{1 - \chi_{H_2O}} \quad (1)$$

where χ_{H_2O} indicates the mole (volume) fraction of water in the products. Thus, the drying factor defined in Eq. (1) accounts for the concentrating effect that removing all of the H₂O has on all of the other constituents of the sample.

Next, the dried sample is mathematically referenced to an equivalent sample with an O₂ concentration of 15%. This results in a dilution factor given as

$$A_2 = \frac{0.209 - 0.15}{0.209 - A_1\chi_{O_2}} \quad (2)$$

where $A_1\chi_{O_2}$ indicates the mole (volume) fraction of O₂ in the *dried* sample. While this step is typically associated with air dilution (i.e., $A_2 < 1$), it should be mentioned that, in applications such as oxy-fuel combustion, this factor may be greater than unity.

Taken together, this gas turbine emissions reporting procedure has the effect of introducing a multiplicative factor equal to the

Table 1 chemical equilibrium results for $T_{ad} = 1800$ K atmospheric and compressed combustion reactions with varying fuel composition

Case	Reactants		Products		
	%H ₂	%CH ₄	%CO ₂	%H ₂ O	%O ₂
Atmospheric	0	100	6.63	13.24	6.20
	25	75	6.02	14.02	6.34
	50	50	5.08	15.21	6.55
	75	25	3.46	17.27	6.93
	100	0	0	21.65	7.72
Compressed	0	100	4.99	9.97	9.81
	25	75	4.52	10.54	9.94
	50	50	3.81	11.41	10.12
	75	25	2.58	12.90	10.44
	100	0	0	16.04	11.12

Percentages are indicated on a molar basis.

product of A_1 and A_2 that is embedded within the reported ppmvdr emissions value as $A_1A_2\chi_i$ for any pollutant species i . To better demonstrate the influence of this sample preparation procedure across a variety of fuels, the upper panel of Fig. 1 plots the contributions of these factors across the different fuel compositions from Table 1. The key point is that the factors introduced by ppmvdr reporting approaches can indicate significantly higher emissions values from H_2 -blended fuels compared to strictly hydrocarbon fuels. It should be emphasized that these results are completely independent of the actual emissions associated with any of the fuels and arise completely due to the drying and dilution of the exhaust gasses. As such, so long as the overall composition of the exhaust gas does not change appreciably, these values vary only weakly for other conditions and fuel blends and are not even restricted to a specific pollutant, though our discussion will mostly emphasize NO_x for illustrative purposes.

In principle, it is unimportant whether or not the factor A_1A_2 is near unity as long as it does not change appreciably depending on the fuel composition. Coincidentally, this property is typically satisfied quite well when comparing among hydrocarbon fuel blends such as may be found across the spectrum of natural gas mixtures. In the context of hydrocarbon fuels, variations in the drying and dilution factors tend to balance each other quite well across a remarkably broad range of conditions, which clearly motivated their original adoption by regulators in the 1970s. For example, the lower panel of Fig. 1 shows that the unblended hydrocarbon fuels considered exhibit a maximum relative difference in A_1A_2 of less than 1.5% for both atmospheric and compressed conditions. This may be the reason why the sample preparation effects emphasized in this paper are not widely appreciated in the combustion community, as such a small discrepancy is unlikely to be relevant in practice. However, this characteristic is not satisfied when comparing hydrogen and hydrocarbon fuels, where Fig. 1 shows a relative difference of up to 40% as the hydrogen fraction

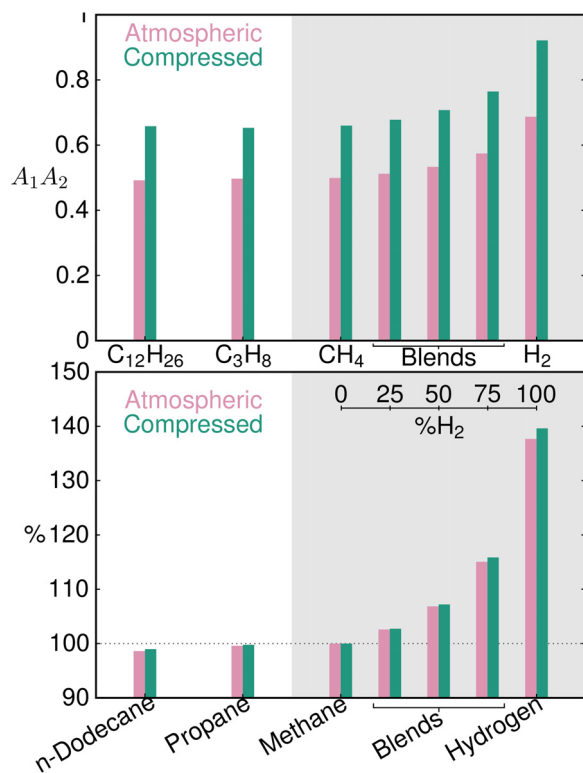


Fig. 1 Combined drying and dilution factors for atmospheric (pink) and compressed (green) combustion cases for three unblended hydrocarbon fuels and a range of CH_4 – H_2 blends at $T_{ad} = 1800$ K (top), and relative differences of these quantities in comparison to those of 100% methane (bottom)

is increased. Indeed, significant fuel effects stemming from the same sample collection procedure should be expected for any comparisons among fuel blends whose combustion products span a substantial range of H_2O and O_2 concentrations. Hydrogen–hydrocarbon blends are one important example of this, but qualitatively similar results may be expected for other alternative fuels, such as blends involving alcohols or NH_3 .

2.2 Consistent Approaches for Cross-Fuel Comparisons of Pollutant Emissions. In general, existing emissions regulations are founded upon concerns over the total amount of pollution being emitted into the atmosphere, as quantified by the mass produced per unit of energy release. Hence, when environmental regulators provide permits specifying emissions allowances in terms of ppmvdr, this quantity can usually be traced to a concrete mass emission rate based on the specific operating parameters of the gas turbine, including its fuel composition. However, perhaps as a result of the ppmvdr values commonly cited on permits, the combustion community has widely adopted ppmvdr values as an *independent* comparative metric within applied emissions research. Section 2.1 has demonstrated that such direct comparisons of ppmvdr emissions values can lead to significant misinterpretations across hydrogen–hydrocarbon fuel blends, as increased ppmvdr values need not be associated with an increased mass emission rate. Thus, this section will discuss three alternative approaches that can be used by the combustion community to directly compare pollutant emissions in a consistent manner across a wide range of fuel blends. It will also provide examples that relate pollutant emissions quantified using each approach to the corresponding ppmvdr values.

2.2.1 True Volume Concentration of Pollutants. The first and simplest approach for quantifying pollutant production across various operating conditions is to use the true (i.e., wet, unreferenced) pollutant concentrations in ppmv. This approach avoids the influences of drying and diluting the exhaust gas sample, thereby removing the factor of A_1A_2 that is present in a ppmvdr value. In practice, this quantity can be directly measured by a gas analyzer with the capability of measuring pollutant concentrations in wet combustion gasses. It can also be straightforwardly determined by separate measurements of the water concentration in the untreated sample and of the pollutant concentration in the dried sample. Yet, since the ppmv emissions value depends only on the composition of the untreated exhaust gas, it does not account for changes in the volumetric flow rate of exhaust or includes any thermodynamic effects associated with the energy conversion process. Hence, while true ppmv values are suitable for direct comparisons of pollutant concentrations across differing exhaust gas streams, additional considerations are necessary to relate these to the mass emission rate of an energy system.

To be clear, the relationship between the true volume concentration of a pollutant (in ppmv) and its ppmvdr value can be completely understood based on Eqs. (1) and (2). Hence, the A_1A_2 values shown in the upper panel of Fig. 1 represent the ratio between the ppmvdr and ppmv values associated with each condition. As a result, ppmvdr values that are already available within the literature may be converted to more easily interpreted true ppmv values so long as information about H_2O and O_2 concentrations is available.

2.2.2 Emissions Mass Referenced to Heat Input. The second approach quantifies emissions based on emitted pollutant mass per unit of thermal energy input. As already mentioned, the first approach does not account for changes in flow rate or thermodynamic effects. Thus, while it is not subject to the confounding influences of drying and diluting the sample, the volumetric approach does not account for a variety of other factors that are also very likely to be important considerations for combustion system emissions. Conversely, the mass-per-heat approach described here includes the effects that the fuel composition has

on the emissions rate through variations in the thermodynamic properties of the reactants and products. These are implicitly accounted for in the mass-per-heat approach because the amount of heat release depends on the fuel composition through the required stoichiometry to achieve a given flame temperature, the heating value of the fuel blend, and the relevant molecular weights, among other factors. Nonetheless, the process of quantifying the emitted mass per unit of thermal energy requires fuel and exhaust flow rate measurements in addition to the volume concentration measurements used in Sec. 2.2.1. In practice, the emitted mass of a pollutant species i per unit of heat input (m_i/Q_{in}) can be related to concentration and volumetric flow rate measurements as follows:

$$\frac{m_i}{Q_{in}} = \frac{\chi_i \rho_i \dot{V}_{exhaust}}{\Delta h_c \rho_{fuel} \dot{V}_{fuel}} \quad (3)$$

where ρ_i and ρ_{fuel} are the respective densities of the pollutant species i and fuel blend, $\dot{V}_{exhaust}$ and \dot{V}_{fuel} are the exhaust and fuel volumetric flow rates, and Δh_c is the fuel blend's heat of combustion. It should be remarked that a notable difference between Eq. (3) and the dimensionless emissions index commonly used for emissions reporting in the aviation sector is the inclusion of Δh_c in the denominator.

The relationship between emissions quantified using the mass-per-heat metric and ppmvdr values can be modeled as follows. First, the thermal energy associated with burning a given mass of fuel is approximated using the lower heating value of the fuel blend. Next, the conversion from a mass basis to a molar basis is performed using the molecular weights of the fuel and the pollutant. This pollutant-to-fuel mole fraction is then converted to a pollutant-to-reactants mole fraction by multiplying the former by the mole fraction of the fuel blend associated with a given T_{ad} . Since combustion processes are not generally equimolar, this mole fraction must then be multiplied by the number of moles of reactants per mole of products to obtain the actual mole fraction of pollutants present in the products. Finally, the actual molar (i.e., volumetric) pollutant concentration in the products is converted to a ppmvdr value using the A_1A_2 factor from the drying and dilution steps described previously. Overall, this process leads to a linear relationship where the constant of proportionality between the pollutant's ppmvdr concentration and its mass per unit of thermal energy is

$$\frac{\text{ppmvdr } i}{(m_i/Q_{in})} = \Delta h_c \left(\frac{M_{fuel}}{M_i} \right) \chi_{fuel} \mu A_1 A_2 \quad (4)$$

where M_{fuel} and M_i are the molecular weights of the fuel and pollutant species i and μ is the mole ratio of reactants to products.

To demonstrate how the mass-per-heat emissions metric described above relates to ppmvdr, example calculations were performed using Eq. (4) with the data from Table 1. In order to remove any ambiguity in the molecular weight, the pollutant species was taken to be NO_2 , a typical surrogate for NO_x . Results for the considered range of fuels are presented in Fig. 2. As before, the results here show a substantial influence of H_2 content in the ppmvdr NO_2 emissions values. The upper panel of Fig. 2 plots the linear relationships between NO_2 emissions reported as a mass-per-heat (abscissa) and ppmvdr NO_2 (ordinate) for the compressed case shown in Table 1. These results once again indicate a notable increase in reported ppmvdr pollutant emissions when using hydrogen. In this case, the discrepancy in ppmvdr values between 100% H_2 fuel and 100% CH_4 fuel at a constant mass-per-heat emission rate is about 36%. Hence, the 4% change between this discrepancy and the 40% variation identified in the previous case may be attributed to thermodynamic effects that were not captured by the constant true ppmv emissions metric. These results are expanded upon in the lower part of Fig. 2, which shows the value of the constant of proportionality between the emissions in terms

of ppmvdr values and those in terms of mass-per-heat values. These results again emphasize how the increases that appear when considering emissions from high % H_2 fuel blends are not pertinent for hydrocarbon fuels, as negligible fuel effects are observed among the hydrocarbons.

2.2.3 Emissions Mass Referenced to Work Output. The third and final approach described in this paper quantifies emissions based on the pollutant mass emitted per unit of useful shaft work from an engine. Therefore, in addition to all of the chemical thermodynamic effects contained in the approach described in Sec. 2.2.2, this metric also includes the influence of the fuel composition on the thermal efficiency of the Brayton cycle, η_T . It is noteworthy that, compared to methane, the Brayton cycle has a slightly higher thermal efficiency for hydrogen fuel blends when run at a fixed firing temperature. This efficiency difference is due to the higher water content of high % H_2 fuels, which increases the specific heat of the exhaust gases relative to the higher % CO_2 exhaust from hydrocarbon fuels. The higher specific heat allows the exhaust gases to hold more enthalpy for a given temperature, altering the balance of power generated in the turbine relative to the power required by the compressor. All else equal, the end result is a more efficient cycle for high % H_2 fuels, and consequently a reduction of the pollutant emissions for a given unit of gas turbine work.

In practice, the emitted mass of a pollutant species i per unit of shaft work output (m_i/W_{out}) can be related to concentration and volumetric flow rate measurements from the exhaust stream and a shaft power measurements as follows:

$$\frac{m_i}{W_{out}} = \frac{\chi_i \rho_i \dot{V}_{exhaust}}{\omega \tau} \quad (5)$$

where ω and τ are the rotation rate and torque of the shaft, respectively. Note that, in circumstances where shaft work

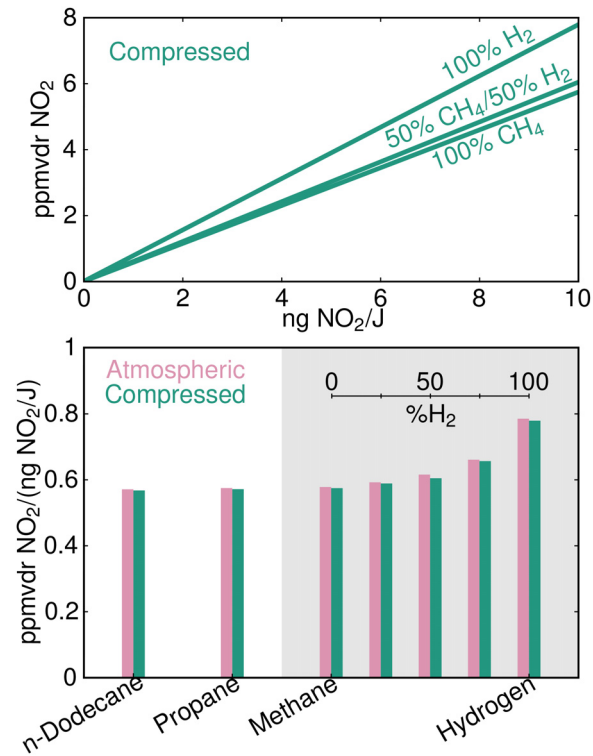


Fig. 2 relation between reported ppmvdr NO_2 and the specific mass production rate per unit of thermal energy input for the indicated blends in the compressed case (top), and comparison of the slope of this linear relation for different fuels and fuel blends at constant T_{ad} (bottom)

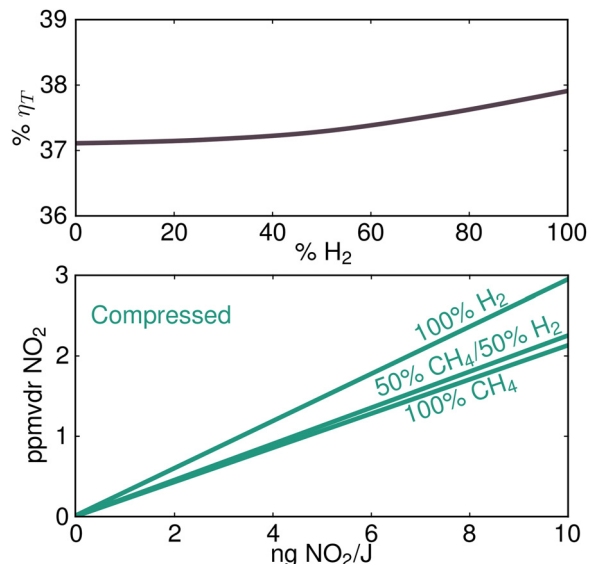


Fig. 3 Brayton cycle efficiency as a function of H_2 content across the range of CH_4 – H_2 blends (top), and the relation between reported ppmvd NO_2 and the mass emissions per unit of shaft work output for the indicated blends in the compressed case (bottom)

measurements are not feasible, Eq. (5) can also be directly related to Eq. (3) using the thermal efficiency since, by definition, $W_{out} = \eta_T Q_{in}$. As a result of this property, a relationship between ppmvd and mass-per-work emissions can be modeled following a similar approach to Eq. (4), but with the efficiency factor included to relate Q_{in} to W_{out} . The resulting relationship is again linear, with a constant of proportionality between the two metrics given by

$$\frac{\text{ppmvd } i}{(m_i/W_{out})} = \eta_T \Delta h_c \left(\frac{M_{fuel}}{M_i} \right) \chi_{fuel} \mu A_1 A_2 \quad (6)$$

To provide an example that quantitatively includes these thermal efficiency impacts, a Brayton cycle calculation was performed for an F-class machine using H_2 – CH_4 fuel blends with a compressor inlet temperature of 300 K, compressor discharge conditions of 17 atm and 700 K, and a turbine inlet temperature of 1600 K. Secondary flow effects were neglected, and the turbine inlet temperature and compressor inlet temperatures were fixed while sweeping

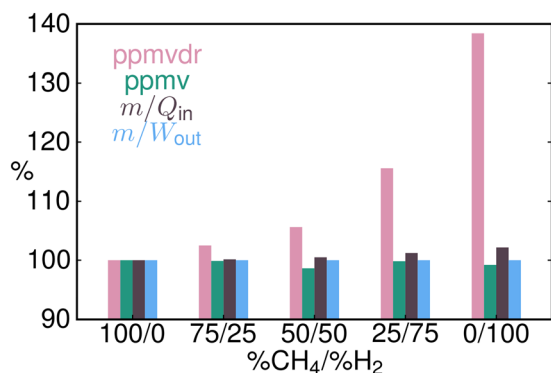


Fig. 4 comparison each of the pollutant reporting approaches discussed in the paper with the ppmvd metric for the compressed case. The plot shows the percentage difference in emissions across CH_4 – H_2 fuel blends relative to the 100% methane case as quantified using each approach under conditions where the emitted mass per unit of work output is constant.

the H_2 content of the fuel. The cycle calculation captured the effects of the varying fuel composition on the resulting heating value and on the composition and properties of the exhaust gas, which was used to extract the thermal efficiency. The results for these cycle calculations are shown in the upper panel of Fig. 3, where the efficiency is observed to rise from about 37% to 38% as H_2 content increases.

To illustrate how this mass-per-work metric for emissions relates to the ppmvd metric, the lower panel of Fig. 3 shows the relationship between the reported emissions based on each approach. Once again, we have chosen NO_2 as an example species to fix the molecular weight of the pollutant. The presented results are based on the equilibrium chemistry data for the compressed case shown in Table 1 combined with the cycle calculations described above. These results reveal that, compared to the mass-per-heat metric described in Sec. 2.2.2, the increased thermal efficiency associated with high- H_2 fuel blends slightly increases the rise in reported ppmvd emissions values relative to 100% CH_4 fuel. More specifically, when the emissions are fixed to a constant value of mass produced per unit of shaft work, a difference of almost 39% appears between 100% CH_4 and 100% H_2 fuels in the reported dry ppmv at 15% O_2 .

2.3 Summary. To summarize our results, we finally examine all of the discussed pollutant reporting metrics in contrast with each other. Figure 4 compares the percentage difference in emissions across CH_4 – H_2 fuel blends relative to the 100% methane case as quantified using each approach under conditions where the emitted mass per unit of work output is constant. It illustrates that the pollutant ppmvd values associated with high % H_2 fuel blends are elevated in comparison to hydrocarbon fuels. As stated throughout the paper, this effect stems from the changing proportions of H_2O and O_2 in the exhaust gas as the fuel's H_2 fraction are varied. Conversely, Fig. 4 indicates only small relative differences among the alternative emissions metrics, as these exclude the drying and dilution procedure associated with determining ppmvd values.

3 Conclusion

While many important scientific and engineering challenges remain to be solved before hydrogen's full potential in the energy sector can come to fruition, this paper has shown that additional issues related to standardized pollutant emissions reporting practices should be reconsidered for this decarbonized future. More specifically, the paper demonstrates how direct comparisons of ppmvd pollutant values, a practice common within the combustion community, can lead to an apparent increase in emissions for H_2 -blended fuels relative to strictly hydrocarbon fuels. While fuel-dependent pollutant formation mechanisms may also play an important role in relative emissions rates, the results emphasize that the increased concentration of water and oxygen in the exhaust gas of high % H_2 fuels is sufficient to exaggerate ppmvd values even without a physical increase in pollutant production.

To remedy this issue, three different metrics for more consistently comparing pollutant emissions across hydrogen–hydrocarbon fuel blends are then evaluated as alternatives to the ppmvd metric. These include: (1) the wet, undiluted pollutant concentration, (2) the emitted pollutant mass normalized by thermal energy input, and (3) the emitted pollutant mass normalized by useful shaft work. Examples are then given across the spectrum of H_2 – CH_4 blends that quantify differences in the apparent emissions of NO_x when evaluated using each of these metrics against the traditional ppmvd approach. For the considered cases, it is shown that ppmvd emissions values vary by 36–40% between 100% hydrogen and 100% methane fuels even when the emission rate is constant with respect to each metric. Considerations associated with implementing such metrics are also discussed. These results highlight the inconsistency of standard ppmvd-based

emissions reporting practices when comparing fuels that exhibit significant differences in exhaust gas composition.

Acknowledgment

The authors are appreciative of Dr. Ray Laster and Dr. Mike Koenig for first raising our awareness of this issue. The authors would also like to thank Mr. Richard Himes and Mr. Aaron Guthrey for their insights and discussions on this topic. Finally, C. D. acknowledges funding for this project from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie Grant Agreement No. 899987.

Nomenclature

A_1 = drying factor
 A_2 = dilution factor
 m_i = mass of species i
 M_i = molecular weight of species i
ppmv = parts per million (volumetric)
ppmvd = dry ppmv
ppmvd_r = dry ppmv at a reference oxygen concentration of 15%
 Q_{in} = thermal energy input
 T_{ad} = adiabatic flame temperature
 \dot{V}_i = volumetric flow rate of species i
 W_{out} = useful shaft work output
 Δh_c = heat of combustion
 η_T = thermal efficiency
 μ = mole ratio of reactants to products

ρ_i = density of species i
 τ = shaft torque
 χ_i = mole (volume) concentration of species i
 ω = shaft rotation rate

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