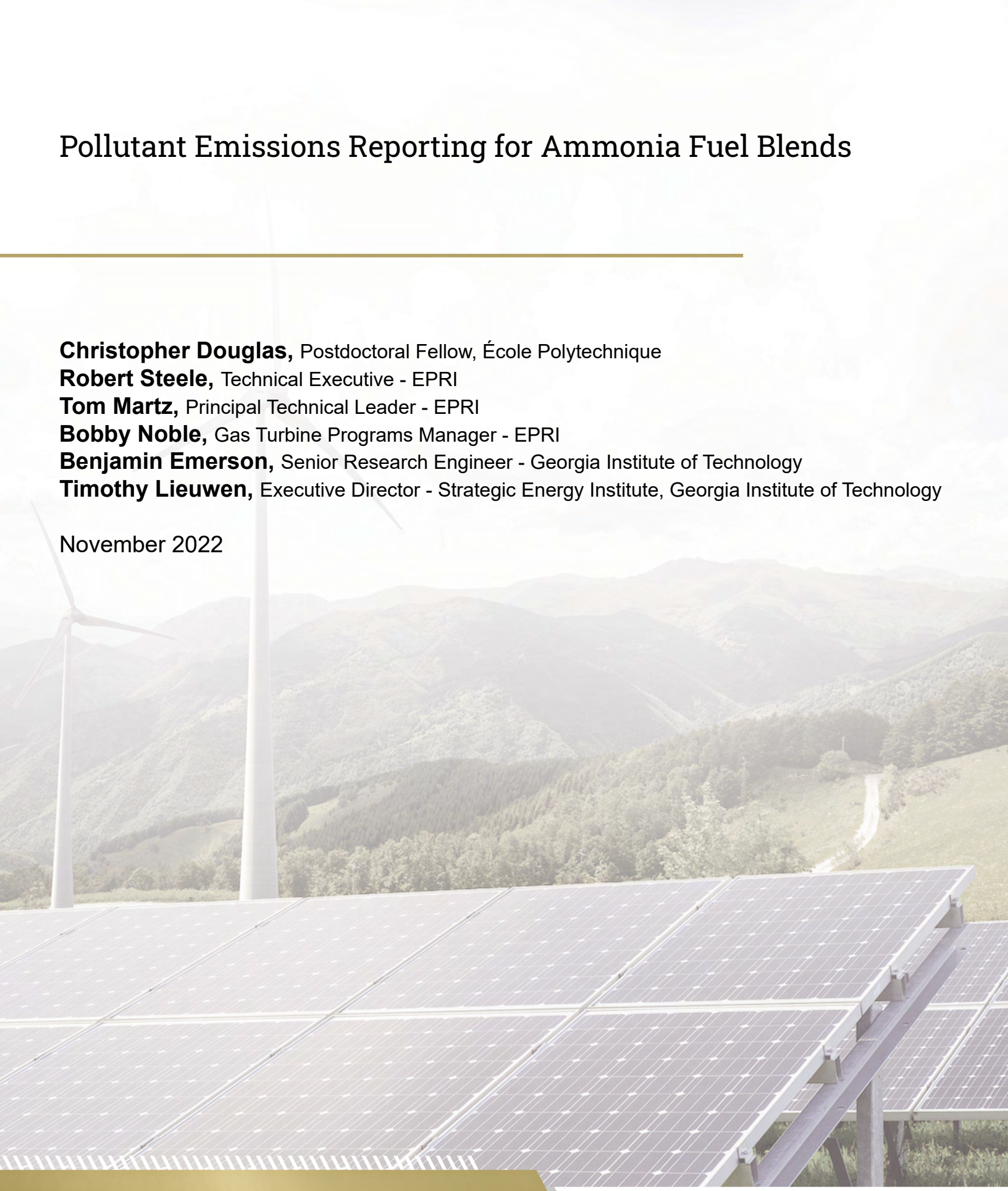
Pollutant Emissions Reporting for Ammonia Fuel Blends

Christopher Douglas, Postdoctoral Fellow, École Polytechnique
Robert Steele, Technical Executive - EPRI
Tom Martz, Principal Technical Leader - EPRI
Bobby Noble, Gas Turbine Programs Manager - EPRI
Benjamin Emerson, Senior Research Engineer - Georgia Institute of Technology
Timothy Lieuwen, Executive Director - Strategic Energy Institute, Georgia Institute of Technology

November 2022



Georgia Tech
Strategic Energy Institute

Executive Summary

To combat carbon dioxide emissions, it is desirable to transition existing combustion systems to carbon-free fuels such as hydrogen and ammonia without negatively impacting air quality. However, quantitatively assessing air quality impacts of pollutants such as NO_x is a nuanced process when comparing emissions across different fuels. Recently, the authors of this study published a separate paper showing that some standardized measurement approaches (i.e., measuring dried exhaust concentration) were inflating pollutant emissions by up to 40% for hydrogen combustion relative to natural gas. In this whitepaper, we extend this analysis to ammonia and cracked ammonia blends, showing that using concentration-based reporting approaches for comparing NO_x from ammonia combustion is appropriate (less than a 3% effect), but can inflate apparent NO_x emissions from fully-cracked ammonia (i.e., an H_2/N_2 fuel blend) by 20%.

Introduction

Climate change concerns are motivating a variety of new strategies to reduce global carbon dioxide (CO_2) emissions. A common theme among many proposals is the establishment of a large-scale green hydrogen economy, where hydrogen (H_2) would be produced from excess renewable energy and transported, stored, and utilized in various applications. In many situations, H_2 can be directly synthesized and oxidized as an energy carrying medium. However, it is also possible to further chemically process H_2 into ammonia (NH_3) which has certain advantages for handling and transport. This ammonia could then be converted back into H_2 or directly utilized. As neither H_2 nor NH_3 contain any carbon atoms, their combustion releases no CO_2 emissions – a key draw for the hydrogen economy concept.

Yet, CO_2 is not the only pollutant of concern among combustion-based energy systems. Nitrogen oxide (NO_x) emissions have a detrimental impact on public respiratory health, and, as such, are regulated in developed countries. For example, the US EPA code part 60 subpart KKKK sets the allowable NO_x emissions for stationary gas turbine operators.

There are two issues associated with NO_x (or any other pollutant, for that matter) emissions from combustion – the first is the actual production rate of NO_x, which is a strong function of combustor design and operating conditions. The second is the development of a consistent approach for quantifying NO_x emissions that allows emissions to be compared across different fuel blends, or at different operating conditions. It is the latter issue which is the focus of this whitepaper. Recently, the authors of this study wrote a paper with a similar goal, focusing on hydrogen--hydrocarbon fuel blends (doi: 10.1115/1.4054949). As detailed in that work, the almost universal approach used in the combustion community for reporting NO_x emissions, which relies on concentration measurements of NO_x and reported in parts per million (ppm) are actually inappropriate for comparing high hydrogen blends to most other fuel emissions, as this approach inflates apparent NO_x emissions. The purpose of this white paper is to provide a companion analysis for ammonia and cracked ammonia blends (i.e., $NH_3/N_2/H_2$).

Pollutant emissions are typically quantified on a volumetric basis based on a standard sample preparation that is designed to avoid influences from changing equivalence and bypass air ratios, and varying levels of steam injection. In this process, the combustion exhaust gases are (1) dried to remove all steam (H_2O) from the sample and (2) diluted to a reference oxygen (O_2) concentration,

typically 15% in the gas turbine community and 3% in the industrial process community. Both of these steps occur prior to measurement, and the reported value is termed “dry ppmv referenced at 15% O_2” (ppmvdr). However, since different fuel blends with equal adiabatic flame temperatures consume different amounts of O_2 and produce different proportions of H_2O, drying and dilution can lead to quantitative differences in reported ppmvdr emissions values even when the emitted mass of the pollutant per unit of energy is identical. As shown by the authors’ earlier work, when comparing pollutant emissions for hydrocarbon and H_2 fuels, this indirect effect turns out to be very significant – representing up to a 40% relative difference in the reported ppmvdr value.

What is the influence of concentration-based dry NO_x reporting methods for NH_3 fuel blends?

To address this question for ammonia we consider fuel blends ranging from 100% methane (CH_4) to 100% NH_3. Constant-pressure equilibrium chemistry calculations were performed at conditions representative of an F-class gas turbine – we specifically used an adiabatic flame temperature of 1800 K for initial reactant conditions of 17 atm and 700 K for results presented here, but these results change only slightly for other conditions. Assuming equal molar pollutant production across the fuel conditions, the resulting relationship between the ppmvdr emissions and the actual ppmv emissions are given in Table 1. These results indicate that the correction resulting from the sample preparation procedure represents less than a 3% relative change. Hence, unlike in hydrogen—methane blends, sample preparation does not significantly affect the interpretation of ppmvdr values for ammonia—methane fuel blends. This is because, compared to a 100% CH_4 flame, the effect of removing steam in high NH_3 blends is compensated by additional O_2 dilution, since the mixture requires a higher equivalence ratio to achieve the same flame temperature. We have confirmed that this general conclusion is also true for ammonia blends involving other hydrocarbons such as propane and n-dodecane, and at other initial conditions and flame temperatures. The same conclusion also holds when assuming equal pollutant mass production per unit of input thermal energy (fuel heating value) as shown in Figure 1.

We should emphasize that we are not saying that ammonia and natural gas produce comparable amounts of NO_x. Rather, we are saying that it is appropriate to compare relative NO_x emissions based upon ppm measurements between the two fuels.

Does “cracking” ammonia influence its indirect ppmvdr emissions?

Because of the high NO_x forming potential of directly burning NH_3, there are also proposals to use catalysts to “crack” ammonia into N_2 and H_2 prior to combustion. To determine the effect of sample preparation on such blends, we consider fuel blends ranging from 100% “cracked” ammonia (½ N_2 + 3/2 H_2) to 100% uncracked ammonia. Using the same calculation approach as above, we then compute the ppmvdr emissions associated with a range of NO_x mass production rates per unit of thermal power. These results are summarized in Figure 1, and indicate that cracking more significantly influences the ppmvdr emissions values, although the magnitude of the difference is less than with pure H_2 (about 20% instead of 40%). The N_2 diluent decreases the molar concentration of dry O_2 in the exhaust, providing a significant dampening effect on the relative correction from the dilution step. This correction is a primary contributor to the increased ppmvdr values in high %H_2 fuels compared to 100% hydrocarbon fuels, so cracked ammonia will generally be influenced less by drying and O_2 dilution compared to pure H_2.

Fuel	Drying factor	15% Dry O_2 factor	Reported ppmvdr per actual ppmv	% difference from 100% CH_4
100% CH_4	1.111	0.5949	0.6609	0
25% NH_3 / 75% CH_4	1.124	0.5898	0.6627	+0.28
50% NH_3 / 50% CH_4	1.143	0.5820	0.6650	+0.62
75% NH_3 / 25% CH_4	1.173	0.5699	0.6686	+1.19
100% NH_3	1.232	0.5484	0.6755	+2.21
100% C_3H_8	1.085	0.6069	0.6583	-0.39
100% $C_{12}H_{26}$	1.073	0.6084	0.6530	-1.18
100% H_2	1.191	0.7735	0.9212	+39.40
100% ½(N_2+3H_2)	1.191	0.6632	0.7896	+19.48

Table 1: Reported Dry NO_x emissions @ 15% O_2 (ppmvdr) for a combustion system operated at various ammonia/methane ratios, relative to the dry NO_x emissions from pure methane. Note that the percent difference shown in the final column does not depend on the chosen %O_2 reference point. Results calculated for 700 K reactants at 17 bar with an adiabatic flame temperature of 1800 K.

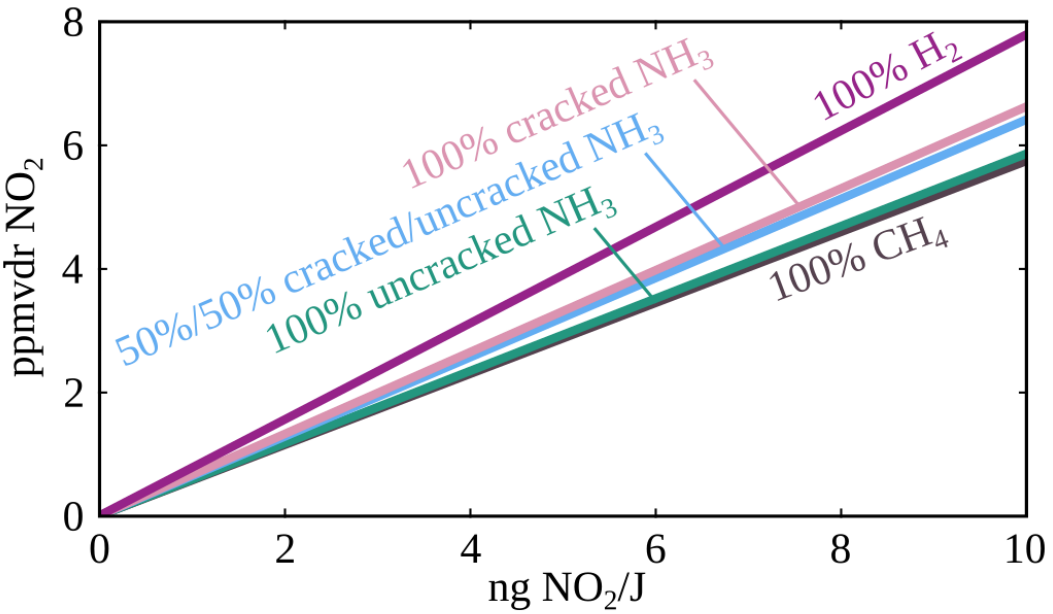


Figure 1: Reported Dry NO_x emissions @ 15% O_2 (ppmvdr) for a combustion system operated at a range of different mass per energy emissions rates using three ammonia-based fuels ranging in composition from 0% to 100% cracked and also 100% CH_4 and 100% H_2 fuel. Results are again calculated for 700 K reactants at 17 bar with an adiabatic flame temperature of 1800 K.

This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No. 899987.

About the Strategic Energy Institute

Few sectors affect the prosperity of every sphere of economic and social life or exert as much direct influence on general technological progress than energy. Concerns surrounding climate change, cost, equity, and security, have brought the development of a clean and diverse energy portfolio to the forefront of the national conversation.

Georgia Tech Strategic Energy Institute

Founded in 2004, the Strategic Energy Institute serves as system integrator for the more than 1000 campus researchers working across the entire energy value chain. We are deeply engaged in building community, developing resources, and projecting thought leadership, all with the aim of marshalling the full resources of Georgia Tech around tackling the tough energy and environmental problems society faces.

As the nation's largest technologically focused university, Georgia Tech is playing an integral role in developing the technologies that are enabling more equitable, lower cost, and cleaner generation, storage, distribution, and utilization of energy. Researchers at Georgia Tech are not just helping to create cleaner, more efficient fuel options or mitigate the environmental impact of conventional energy supplies, they are creating better performing, more economically viable energy options.

About EPRI

EPRI

EPRI conducts research and development relating to the generation, delivery, and use of electricity for the benefit of the public. An independent, nonprofit organization, EPRI brings together its scientists and engineers as well as experts from academia and industry to help address challenges in electricity, including reliability, efficiency, affordability, health, safety, and the environment. EPRI also provides technology, policy, and economic analyses to drive long-range research and development planning, and supports research in emerging technologies.

EPRI's trusted experts collaborate with more than 450 companies in 45 countries, driving innovation to ensure the public has clean, safe, reliable, affordable, and equitable access to electricity across the globe. EPRI's principal offices and laboratories are located in Palo Alto, Calif.; Charlotte, N.C.; Knoxville, Tenn.; Dallas, Texas; Lenox, Mass.; and Washington, D.C.