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Proceedings of Combustion Institute – Canadian Section
Spring Technical Meeting
University of Waterloo
May 10-12, 2016

Emissions of Nitrogen Oxides from Turbulent Non-Premixed Flames: A Comparison to Current Emission Factors and Scaling Laws

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Abstract

Emission of nitrogen oxides (NOx, sum of nitric oxide and nitrogen dioxide) were measured from turbulent non-premixed flames of pure propane and methane, and an alkane mixture of C1-C4. Results were compared with currently accessible emission factors and source data from governmental agencies in Canada, the United States, South America, and Europe. The linear relationship between NOx emissions and mass, volume, and energy content of flare gas inherently assumed in available emission factors generally matched the trends in the current data, but variations in fuel composition could lead to an underestimation of emissions. NOx emissions were underestimated by up to 24% from methane flames when using a mass-based emission factor, by up to 54% from propane flames using a volume-based factor, and by up to 12% for methane flames using a heat-release-based factor. A theoretical non-linear relationship between NOx emission and volume flow rate parameters from the literature was examined and found to perform no better than the linear relations of current emission factors. A significant expansion of experimental data and conditions is required to fully comprehend the complexities of NOx formation in non-premixed turbulent flames, and to the develop a robust NOx emissions models necessary for gas flares used in the energy industry.

1. Introduction

Flaring is the practice of combusting unwanted or uneconomically viable flammable gases and is common in a multitude of industries. Recent satellite data suggest that approximately 140 billion cubic meters of gas are flared annually, amounting to 4% of global natural gas production [1,2]. Regulations in the United States and Canada for the upstream oil and gas industry promote flaring over venting as a means to reducing greenhouse gas emissions [3,4]. However, combustion emissions are still of concern. In addition to carbon dioxide emissions (CO_2), small quantities of unburned or partially combusted fuel (i.e. volatile organic compounds, VOCs) and criteria pollutants like carbon monoxide (CO), nitrogen oxides (NOx), sulfur oxides (SOx, in the case of sour gas), and black carbon (BC, a component of soot) may be emitted. These species have significant human health and environmental impacts: NOx and SOx lead to acid rain [5]; VOCs, NOx, and soot promote the production of smog and ground-level ozone [5]; and BC is linked to respiratory illnesses and fatality [6]. Quantifying emission factors for these combustion products is vital to understanding the affect flaring has on the global climate and human health. Independent studies of wide ranges of fuels, flow, and flame regimes to determine robust NOx emission factors are critically lacking – the focus of this paper is to compare experimental yields of NOx with available emission factors and scaling laws to determine their applicability to a variety of flow conditions and fuels.

1.1 NOx Emission Factors for Flaring

Current emission factors used or suggested by governmental agencies are single-value parameters linearly relating the mass emissions of NOx to the mass, volume, or energy of the flare gas. The USEPA provides an emission factor of 0.068 lb NOx per 10^6 BTU of gas flared [7]. Available documentation indicates that this value is based upon a single study conducted in 1983 on a large-scale flare of crude propylene (80% propylene, 20% propane) [8].

The Canadian Association of Petroleum producers (CAPP) suggests an emission factor of 1.345 kg NOx per 10^3 m^3 of fuel flared which is based exclusively on the emission factor from the USEPA using assumed heating value of 45 MJ/m^3 [7,9]. In South America, ARPEL (Regional Association of Oil, Gas and Biofuels Sector Companies in Latin America and the Caribbean) published a report co-written by a Canadian environmental consulting agency with funding from the Canadian International Development Agency, suggesting an emission factor based upon [9] and [7]

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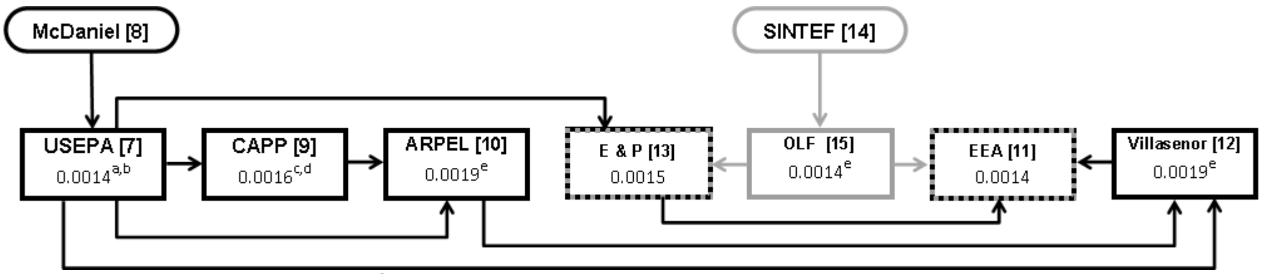
of 0.0016 kg NOx per m^3 sweet gas [10]. In Europe, the EEA suggests a factor of 1.4 kg NOx per metric ton of flare gas (sour, upstream oil and gas extraction flared specifically) [11], which was calculated using three reports: Villasenor et al. [12], a 1994 study by the Oil Industry International Exploration and Production Forum (E&P) [13], and a report by the Foundation for Scientific and Industrial Research (SINTEF) commissioned by the Norwegian Oil and Gas Industry (OLF) [14,15]. The factor proposed by [12] is the geometric mean of emission factors from [7] and [10] and [13] references emission factors from [7] and [14]. [14] re-analyzed data available in the literature and conducted field experiments on two off-shore flares to determine an emission factor of 1.2 kg NOx per 10^3 m^3 flare gas. Figure 1 summarizes the web of references for each emission factor discussed. There are essentially only two sources of measurement data for the myriad available emission factors. Black outlines represent emission factors based solely on [7], and light grey from [14]. Dotted outlined represents emission factors based upon the two aforementioned independent studies.



[a] Assumed flare gas density: 1.90 kg/m^3 (based on flare gas compositions in [8])
[b] Assumed flare gas higher heating value: 93 MJ/m^3 (as stated in [7])
[c] Assumed heating value of 45 MJ/m^3 (as stated in CAPP documentation[9])
[d] Assumed flare gas density: 0.83 kg/m^3 (back-calculated from [9] and [7] with given unit conversions)
[e] Assumed flare gas density: 0.85 kg/m^3

Figure 1. Sources of available NOx emission factors converted units of kg NOx per kg flare gas

1.2 NOx Scaling Laws

Rokke et al. [16] scaled an emission index (yield of NOx multiplied by a factor of exit velocity, density, and burner diameter) with the Froude number (defined as $Fr = u_0^2/gd_0$ where the subscript '0' denotes properties at the burner exit, u is the velocity of the gas, d is the diameter of the burner, and g acceleration due to gravity). This relation presented in eq. (1) and was derived with a 15-step reduced mechanism for NO formation via thermal, prompt, and nitrous oxide routes [16]. Noting the common terms on each side of eq. (1), this scaling law reduces to a simple non-linear function of NOx mass emission rate, $\dot{m}_{NO_x}$ [g/s], with volume flow rate of flare gas, Q [m^3/s], as shown in eq. (2).

$$Y_{NO_x}\left(\rho_0 \frac{u_0}{d_0}\right) \approx 44 \Bigg(\underbrace{\frac{u_0^2}{gd_0}}_{Fr}\Bigg)^{3/5} \quad (1)$$

$$\dot{m}_{NO_x} \approx 0.047 Q^{1.2} \quad (2)$$

where Y_{NO_x} is NOx yield in [g NOx/kg flare gas], ρ_0 is the density at the burner exit in [kg/m^3], $\dot{m}_{NO_x}$ is the mass emission rate of NOx in [g/s], and Q is the volume flow rate of flare gas in [10^3 m^3/s]. Data in the present study will be compared to the scaling relation of eq. (2) derived from [16], and a the simple emission factors presented above.

2. Experimental Setup and Experimental Methods

Experiments were performed at the Carleton University Lab-Scale Flare (CLSF) facility at which custom hydrocarbon and inert fuel mixtures can be flared at up 400 SLPM. Figure 2 shows the burner which sits in a 1.9 m deep concrete pit. Two concentric settling screens and additional air supply vents surround the burner to reduce disturbances to the flame. Centred 3.14 m above the flame, a large fume hood captures combustion product species and dilution air. Samples are collected 10 m downstream where gas- and solid-phase combustion product analysis equipment continuously monitor concentrations of carbon dioxide, carbon monoxide, nitrogen oxides, methane, acetylene, additional higher hydrocarbons (C2+), and soot. Emission yields are calculated as in [17].

Tests conducted for this report examine three potential variables affecting NOx yields: fuel chemistry, flow rate, and burner diameter. Pure methane and propane were flared at three flowrates each at a single burner diameter. A hydrocarbon mixture (heavy-4) of 74.54% methane, 15.47% ethane, 6.83% propane, and 3.16% butane was flared at three flowrates each for three burner diameters. The composition of this mixture is based on [18] – a study of flare gas composition in western Canada. Table 1 below summarizes the experiments performed.

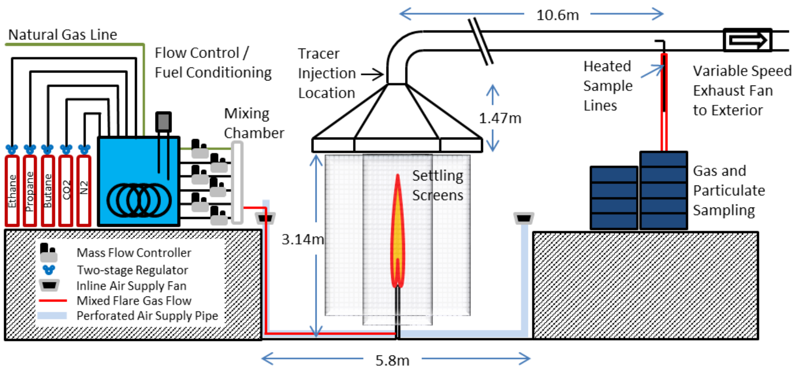


Figure 2. Carleton Lab-Scale Flare Facility

Table 1. Experimental Matrix

Burner Ø [mm]	**Fuel Type and Flow Rate [SLPM]** *Methane*	*Propane*	*Heavy-4*
38.1			61.56 102.61 150.49
50.8	60.80 109.45 182.41	12.16 30.40 60.80	60.80 109.45 182.41
76.2			27.36 68.41 136.81

3. Results and Discussion

Figure 3(a)-(c) presents the experimental results of NOx yield on three bases: mass, volume, and energy. Overlaid on the data are lines representing the emission factors previously discussed in their respective published units. Examining Figure 3(a), the data appear to be separated by fuel chemistry by as much as 18% from the average: a linear fit to methane data produces a slope of 0.0017 kg NOx per kg fuel ($R^2 = 0.998$); propane, a slope of 0.0013 kg NOx per kg fuel ($R^2 = 0.996$), and combining results of all burner diameters, heavy-4 fit a slope of 0.0016 kg NOx per kg flare gas ($R^2 = 0.990$). Less significant differences in slope were seen in flares of heavy-4 fuel of varying burner diameter (~12% from the mean). Relative to the current measured data, NOx emissions from pure methane flares are underestimated by 24% using the EEA emission factor [11] and by 19% using the E&P emission factor [13].

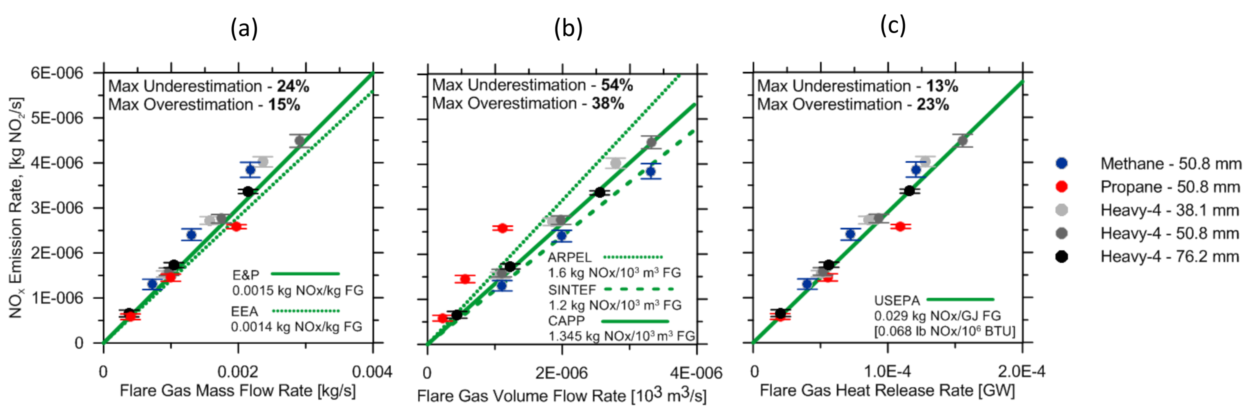


Figure 3. Emission rate of NOx versus flare gas flow rate in (a) mass, (b) volume, and (c) heat release. Green lines indicate emission factors legislated or suggested by governmental agencies in their published units.

When the data are plotted on a volume basis in Figure *3*(b), linear fits for each individual fuel composition are good ($R^2 > 0.99$), but fits for each fuel chemistries have significant differences in slope. The propane data follows a slope of 2.22 kg NOx per 10^3 m^3 of flare gas, compared to methane at 1.14 kg NOx per 10^3 m^3 of flare gas. The three emission factors discussed that published in mass of NOx per volume of flare gas (CAPP, ARPEL, and SINTEF [9,10,14]) align well with methane-based fuels, but underestimate NOx emissions from propane flames by up to 54%.

Data presented in terms of heat release rate in Figure 3(c) appears to slightly collapse the differences in slope due to fuel-chemistry to a maximum deviation of approximately 17% from the mean. The emission factor published by the USEPA [7] aligns with the average slope for all the data – though for the cases examined in this study, the USEPA factor underestimates emissions from methane flares by up to 13%, while overestimating emission from propane flames by up to 23%.

The non-linear relationship between NOx emission rate and flow rate proposed by [16] is presented in the format of the original publication in Figure 4(a) with data from the present study. Propane data appears to align well with the theoretical scaling law, eq. (1), though methane-based fuels appears to fall below the curve. Figure 4(b) re-plots the proposed scaling relation in mass emission rate of NOx with volume flow rate and the rearranged scaling law presented in eq. (2). Current emission factors published in volume-based units are also included. It is clear that for the data collected in this study, the appearance of a well-fitting relationship between NOx emissions and Froude number is perhaps a figment of the common terms and logarithmic scale on both axes of Figure 4(a). Further, comparing this scaling relation to the emission factors, it is clear that the simple power law scaling relation with flow rate does not improve upon the currently utilized linearly scaled emission factors.

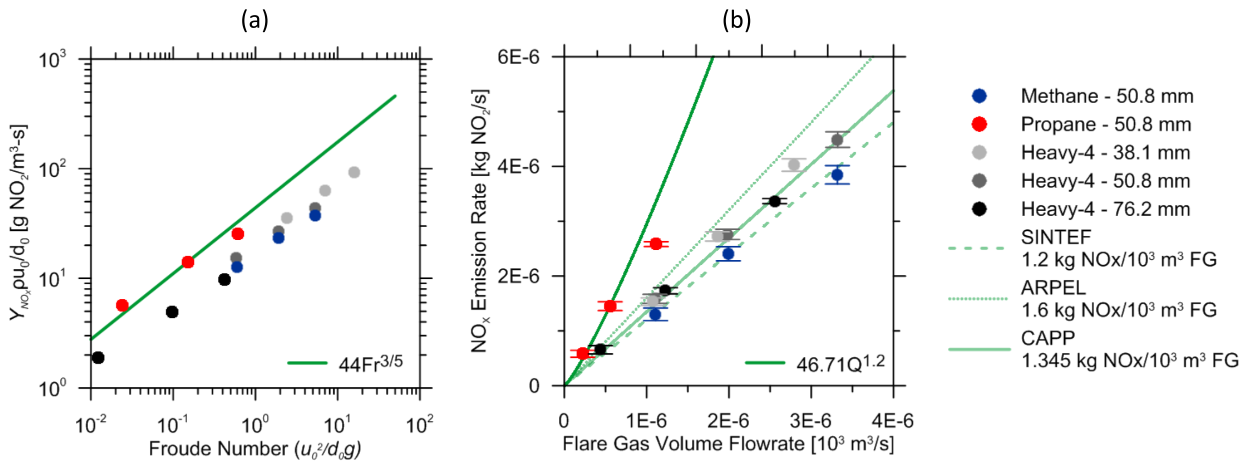


Figure 4. Proposed scaling law of [16] plotted in (a) as presented in original publication and rearranged in (b) in terms of flare gas volume flowrate.

Current emission factors inherently assume a linear relationship between NOx emission rates and flow rates in volume, mass, or energy basis. It appears that the flowrates and diameters examined, this assumption is reasonable for any one specific fuel mixture. However, the slopes of NOx emission vs. flares gas flow differ by fuel type leading to significant over and underestimations in NOx emission estimates. Of the discussed emission factors from various governmental agencies and within the limits of the measured data in the present work, emission factors presented in a mass of NOx per energy content of fuel best estimates emissions with a maximum error of +12%/-23%. However, a broader range of flare gas mixtures and conditions could be expected to give larger errors. As the thermal mechanism for NOx is a dominant pathway for formation [19,20], flame temperature and radiant losses due to soot production likely need to play a large part in developing better models for predicting NOx emissions from turbulent non-premixed flames and flares.

4. Conclusions

NOx emissions from flares of methane, propane, and natural gas mixtures from 38.1, 50.8, and 76.2 mm burner diameters were examined and compared to current emission factors of agencies in North and South America and Europe. Within the relatively limited data set, NOx emissions scaled linearly with flare gas flow rate (on a volume-, mass-, and energy-basis) for any one fuel composition; however, no simple relation could predict emissions over a range of different fuels. A proposed scaling law in the literature for a NOx emission index with Froude number was found to reduce to a simple non-linear relation between NOx mass emission rate and volume flow rate. This relation predicted NOx emissions no better than current emission factors within the fuels, flowrates, and diameters examined.

Additional tests to expand ranges flow rate, burner diameter, and fuel chemistry, and consideration of soot formation and flame temperature will significantly aid the pursuit of a robust emission factor for NOx emissions from flares.

Acknowledgements
Support for this project was provided by the Petroleum Technology Alliance of Canada (PTAC), Natural Resources Canada (Canmet ENERGY-Devon), and Natural Sciences and Engineering Research Council of Canada (NSERC).

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