Methodology and Experiments to Determine Soot and NO_x Yields from a Vertical Lab-Scale Flare Burning Alkane-Mixtures and Ethylene

By

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Abstract

Species yields and combustion efficiency of lab-scale flares, turbulent non-premixed buoyant flames, were measured. A new facility was constructed allowing gas mixtures to be burned on 38.1 to 76.2 mm diameter flares at flow rates up to 410 standard litres per minute. A methodology was developed to quantify species yields and combustion efficiency within calculated uncertainties. Results showed combustion efficiencies greater than 97.8% in all cases, with up to 90% of the non-CO₂ carbon emitted as soot. Soot yields were heavily dependent on flare gas chemistry, ranging from an average of $7.34 \cdot 10^{-5}$ kg-soot/kg-flare-gas for methane tests to $1.20 \cdot 10^{-2}$ kg-soot/kg-flare-gas for ethylene tests. NO_x data suggest that average mass yield per energy content of the flare gas is $3.76 \cdot 10^{-2}$ kg-NO_x/GJ and is independent of exit conditions and fuel chemistry for the range of fuels considered. Results are compared with published soot and NO_x emission factors and potential scaling methods are discussed.

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Nomenclature

Latin Symbols	Description	Units	First Use Eq.	Pg.
ARPEL	Asociacion Regional de Empresas de Petroleo y Gas Natural en Latino America y el Caribe			6
BC	Black Carbon			3
CAPP	Canadian Association of Petroleum Producers			5
CV	Control Volume			54
d	Diameter	m		14
$DIAL$	Differential Absorption Lidar			29
DRE	Destruction Removal Efficiency	%	(3.2)	53
DSCF	Dry Standard Cubic Feet	ft ³ /min		6
E_{NOx}	NO _x Yield	kg/kg	(1.6)	22
EEA	European Environment Agency			8
E&P	Exploration and Production			7
f_s	Stoichiometric Mixture Fraction			14
f_v	Soot volume fraction	ppb _v		67
Fr	Froude Number		(1.4)	15
Fr_f	Fire Froude number		(1.3)	13
Fr_g	Global Froude number		(1.2)	13
$FTIR$	Fourier Transform Infrared Spectrometer			40
g	Gravitational Constant	9.81 m/s ²		14
GGFR	Global Gas Flaring Reduction			4
GHG	Greenhouse Gas			3
GWP	Global Warming Potential			3
HHV	Higher Heating Value	MJ/m ³		7
ID	Inside diameter	mm		33
LGR	Los Gatos Reasearch			40
LII	Laser Induced Incandescence			43
M	Molar mass	kg/kmol		60
$\dot{m}$	Mass flow rate	kg/s		54
$mean$	Mean of data set			98
n	Number of points of data set			98
$\dot{n}$	Mole flow rate	kmol/s		57
NAEI	National Atmospheric Emissions Inventory			8
NPRI	National Pollutant Release Inventory			5
OLF	Norwegian Oil Industry Association			8

Latin Symbols	Description	Units	First Use	
			Eq.	Pg.
P	Pressure	Pa		68
PM	Particulate Matter			4
$\dot{Q}$	Flow rate	m ³ /s		67
Re	Reynolds number		(1.1)	13
R_u	Universal gas constant	8314 J/kmol-K		69
RSS	Residual sum of squares			103
SCF	Standard Cubic Feet	ft ³ /min		6
SLPM	Standard Litres per Minute	L/min		32
SVF	Soot Volume Fraction			43
T	Temperature	K		14
ΔT_f	Flame Characteristic Temperature Rise	K		14
TCEQ	Texas Commision on Environmental Quality			28
u	Velocity	m/s		14
UKOOA	United Kingdom Offshore Operator Association			8
US EPA	United States Environmental Protection Agency			4
X	Mole fraction, concentration			57
Y	Mass fraction			55

Other Symbols	Description	Units	First Use	
			Eq.	Pg.
ρ	Density	kg/m ³		14
μ	Dynamic Viscosity	kg/m-s		14
η	Combustion Efficiency	%	(3.1)	52
$\#_{c,i}$	Carbon number of species i			59
σ	Standard deviation of data set			98

Subscripts	Description	First Use	
		Eq.	Pg.
<i>0</i>	Refers to conditions at the burner exit		14
<i>2.5</i>	Particulate matter (PM) less than 2.5 nanometres size		4
<i>10</i>	Particulate matter (PM) less than 10 nanometres size		8
∞	Refers to ambient conditions		14
<i>ad</i>	Refers to adiabatic conditions		14
<i>combusted</i>	Refers to portion of flare species combusted		72
<i>combustion</i>	Refers to portion of air required for stoichiometric		54
<i>air</i>	combustion of flare gas		
<i>dilution air</i>	Refers to portion of air diluting the products of combustion		54
<i>FG</i>	Refers to flare gas		54
<i>FL</i>	Refers to flare liquid		72
<i>i</i>	Refers to a given species		53
<i>inert</i>	Refers to inert species in the flare gas		54
<i>measured</i>	Refers to conditions measured at LII, specifically		68
	temperature and SVF		
<i>plume</i>	Refers to diluted plume, sum of products and dilution air		54
<i>produced</i>	Refers to production rate due to chemical reactions		54
<i>tracer</i>	Refers to the tracer gas acetylene		71

Preface

This thesis includes an integrated article that has been published to a scholarly journal:

Corbin, DJ, MR Johnson (2014) Detailed Expressions and Methodologies for Measuring Flare Combustion Efficiency, Species Emission Rates, and Associated Uncertainties, *Industrial & Engineering Chemistry Research* 53 (49), pp 19359–19369. doi: 10.1021/ie502914k

The article is included in its entirety as Chapter 3 with the corresponding supplemental material included as Appendix A. The article details the methodology used to produce the results presented in this thesis. The article is reproduced as published with modifications to formatting and the numbering of sections, figures, tables and equations. The preferred method of citing this work from the thesis is to directly reference the published article if possible. The article is copyright of the American Chemical Society and subject to their Journal Publishing Agreement which permits use of authored work by the author in a thesis.

Student Statement Regarding Student Involvement

I, Darcy Corbin, was fully involved and responsible for setting up equipment, obtaining data, analyzing results, and writing the first drafts of the material presented in the article noted above and included as Chapter 3 of the thesis.

Darcy J Corbin

Supervisor Statement Regarding Student Involvement

The student, Darcy Corbin, was fully involved and responsible for setting up equipment, obtaining data, analyzing results, and writing the first drafts of the material presented in the article noted above and included as Chapter 3 of the thesis.

Matthew R Johnson

Chapter 1

Introduction

1.1 Background & Literature Review

Flaring is the practice of waste gas disposal through the process of combustion. During oil extraction, if it is uneconomical to capture the associated gas products, they are either directly vented to the atmosphere or flared. Because raw methane (CH_4), the main component in waste gas streams in the upstream energy industry, has a 100-year time-horizon Global Warming Potential (GWP) $30^1\text{--}36^2$ times higher than carbon dioxide (CO_2) on a mass basis (Myhre et al., 2013), flaring can reduce greenhouse gas (GHG) emissions relative to venting. Factoring the differences in molecular masses between CO_2 and CH_4 , flaring one unit of CH_4 produces 10.9–13.1 times less CO_2 equivalent GHG emissions than direct venting of that same gas. This highlights the importance of the combustion process in effectively converting methane and other hydrocarbon constituents to carbon dioxide (CO_2). Since in practice hydrocarbon combustion is not perfect, black carbon (BC), unburned or reformed hydrocarbons, and other toxic air pollutants are generally produced via the flaring process. These products of incomplete combustion have important effects on both public health and the environment at large (US EPA, 2012).

¹ Value for ‘fossil methane’ without climate-carbon feedbacks

² Value for ‘fossil methane’ with climate-carbon feedbacks

Efforts funded by the World Bank Global Gas Flaring Reduction (GGFR) partnership using satellite observations to estimate gas flaring volumes indicate global gas flaring exceeded 133 billion cubic metres in 2010, and flaring volumes in Canada exceeding 2 billion cubic metres in the same year (NGDC, 2014). Studies suggest that the volume of natural gas flared globally is about 5% of world consumption (US EPA, 2012). Flaring activities can be categorized into three rough categories: emergency flaring, process flaring and production flaring (Johnson, Kostiuk, et al., 2001). Emergency flaring encompasses unexpected releases of combustible gas due to a variety of potential causes and generally entails high volumes of gas being flared over short durations of time. Process flaring is primarily found in downstream oil or gas processing facilities, where waste products of varying composition may be continuously flared at relatively low flow rates. Production flaring includes both short term flaring during commissioning of new gas wells (well test flaring) and continuous flaring of unusable solution gas over the lifetime of an oil-well. Solution gas flares are the primary focus of the current work, and comprise the majority of flaring activity in the Alberta upstream oil and gas industry (Johnson, Kostiuk, et al., 2001).

Solution gas flares, as illustrated schematically in Figure 1.1, are generally described as simple pipe-flares, in which a straight length of pipe nominally between 3 – 10 inches in diameter extends vertically into the air in the order of 10 meters (Johnson, Kostiuk, et al., 2001). The pipe exit may contain a simple wind shroud (usually a larger diameter, open-ended cylinder encircling the exit and aligned with the pipe) or may be unmodified. These simple designs are in contrast with large, multi-burner engineered tips which are more common in process flaring applications. Additionally, common

practices such as steam- or air-assisted flaring (where pressurized steam or air are injected into the combustion zone to promote mixing and suppress soot formation) are generally not implemented in the remote locations which are characteristic of upstream oil and gas flaring. Due to the simple design, combustion is carried out under non-premixed conditions. Flare gas absent of an oxidizer is delivered to the tip of the flare where it exits at near atmospheric conditions in terms of temperature and pressure. An electronic ignitor or a pilot flame may be installed at the tip to ensure continuous ignition of the flared gas.

Figure 1.1: Schematic of generic solution gas typical of the Alberta upstream oil and gas industry

The importance of BC as an emission from flaring is a major motivation for the current work. Black carbon in the atmosphere is believed to be the 2nd most important climate forcer after CO₂ (Bond et al., 2013). While the fraction of global BC emissions

attributable to gas flaring may be small (< 3%), the majority of flaring activity takes place in sensitive northern latitudes (Stohl et al., 2013). Flaring is the largest anthropogenic source of BC north of 60° N (2nd to natural biomass combustion overall) and estimated as the single largest source north of 66° N (i.e. north of the Arctic circle). Simulations suggest that BC from flaring constitutes 42% of the annual mean BC level in the Arctic (Stohl et al., 2013) making it the dominant source in the region.

Particulate matter (PM) with a diameter less than 2.5 micrometres (PM_{2.5}) has been a component of the National Ambient Air Quality Standards issued by the United States Environmental Protection Agency (US EPA) since its differentiation from larger PM in 1997. The US EPA defines black carbon as synonymous with elemental carbon, soot, and light-absorbing carbon and distinct from both organic and carbonate carbon forms (US EPA, 2004). In recent years, it has been suggested that in addition to the acknowledgement of PM_{2.5} as a significant health hazard, BC specifically should be investigated as an equal or greater hazard due to recent developments in monitoring technology. Specifically, BC can be causally linked to lung cancer and cardiovascular mortality, and possibly adverse birth and nervous system effects (Grahame et al., 2014).

1.2 Emissions Estimates

Estimates of flare-generated pollutant emissions are generally calculated based on simple emission factors. For example, the Canadian Association of Petroleum Producers (CAPP) recommends single-valued emission factors for various species (particulate, NO_x, CO) for use in reporting flare-generated emissions to the Canadian National Pollutant Release Inventory (NPRI). As further summarized in the following section, these emission factors are in general overly simplified and of questionable validity.

Poorly estimated emission magnitudes adversely impact the accuracy of national and international pollutant inventories, and impedes sound policy decisions. Better emissions quantification remains a critical experimental research challenge. Numerous studies emphasize the necessity of continued work in the quantification of emissions and development of emission factors for flaring activities in particular (Stohl et al., 2013; US EPA, 2012; Arctic Council, 2011).

1.2.1 Current Emission Factors for Flares

A review of available emission factors in the literature has shown that most are ultimately sourced from a very limited number of primary studies and published values. The most accessible emission factor data for flaring activity in North America is published by the US EPA and CAPP. Other emission factors are available for flaring activity in Latin America, Europe, and the UK. Emission factors discussed in this section are summarized in Table 1.1, which considers soot emission factors, and Table 1.2, which considers NO_x emission factors. The tables report the emission factors both in the units presented in the relevant cited source document, and in a common set units as calculated by the author. Also listed is the composition of the flare gas used in the development of each factor.

The US EPA provides emission factors for flaring from a number of sources. AP 42 compiles pollutant emission factors for stationary sources and provides two subsections relevant to flaring. Landfill gas flaring is outlined in Section 2.4 (US EPA, 1998) of the AP 42 document and includes a soot emission factor of 17 lb/10⁶ dry standard cubic feet (DSCF) of methane and a NO_x emission factor of 40 lb/10⁶ DSCF of methane. These numbers are attributed to testing on enclosed flares (US EPA, 1998). Section 13.5 (US EPA, 1995) of AP 42 covers industrial flares and provides four single-

value soot emission values ranging from 0-274 $\mu\text{g/L}$ of exhaust product for flares ranging from non-smoking to heavily-smoking operating conditions. A single NO_x emission factor of $0.068 \text{ lb}/10^6 \text{ Btu}$ of flared gas is also provided. These soot and NO_x factors are cited from flare experiments (McDaniel, 1983) in which crude propylene was used as fuel. A third set of emission factors available from the US EPA online WebFIRE database (US EPA, 2014) suggests values of $53 \text{ lb}/10^6$ standard cubic feet (SCF) for soot and $28.3 \text{ lb}/10^6 \text{ SCF}$ for NO_x . These values are derived from a confidential US EPA report (US EPA, 1991) and reference a landfill gas flare as a data source. These data are the basis for the emission factors recommended in the CAPP NPRI.

The Asociacion Regional de Empresas de Petroleo y Gas Natural en Latino America y el Caribe (ARPEL) publishes emission factors for solution gas³ combustion from heavy crude oil primary (sweet) and thermal (sour) facilities, as well as for steam assisted flaring at gas plants (Franklin and Leahey, 1998). These values are derived from documents and presentations by CAPP, US EPA and the now defunct Canadian Ministry of Energy, Mines and Resources. Separate single-valued soot emission factors of 0.0023 and $0.0023 \text{ kg}/\text{m}^3$ are suggested for sweet and sour crude oil facilities respectively. For steam-assisted flaring at gas facilities, a factor of 43.0 t/PJ is recommended. The NO_x emission factor for flaring associated with crude oil facilities is $0.0016 \text{ kg}/\text{m}^3$, while for steam-assisted flaring at gas facilities it is over fifty percent greater at 59.0 t/PJ of fired gas.

³ Defined here as gas that is co-produced with oil and/or gas released from oil when it is reduced to atmospheric pressures from formation pressures.

In their guidance document for reporting to the NPRI, CAPP provides single-valued emission factors for soot and NO_x (CAPP, 2007). Both emission factors are derived from US EPA emission factors; the soot emission factor is attributed to a confidential US EPA report (US EPA, 1991) investigating emissions from landfill gas flaring, and the NO_x emission factor is attributed to AP 42 Section 13.5 (US EPA, 1995). The CAPP soot emission factor of 2.5632 kg/1000 m³ (significant figures as reported) is scaled to a nominal higher heating value (HHV) of 45 MJ/m³ for upstream oil and gas (UOG) flaring from the US EPA factor for landfill gas which has an assumed HHV of 15 MJ/m³ and is presented on a per volume basis. The NO_x emission factor of 1.345 kg/1000 m³ was converted from the US EPA factor which is presented on a per energy content basis also using a nominal HHV of 45 MJ/m³.

The Exploration & Production (E&P) Forum (Shah and Pope, 1994) report provides a gas flaring emission factor for NO_x only. The reported value of 0.0015 t/t flared gas is based on emission factors from three primary sources, although it is not clear how the final value was calculated. The sources for the NO_x emission factor include a Norwegian Oil Industry Association (OLF) report (OLF Environmental Programme, 1991) and a United Kingdom Offshore Operator Association (UKOOA) report (UKOOA, 1993) neither of which could be found, as well as E&P Forum internal data which shares a value with the work of McDaniel (1983).

The European Environment Agency (EEA) publishes regular updates of emission factors for a variety of industries and activities. The most recent publication (Trozzi, 2013) provides soot and NO_x emission factors relevant to flaring in oil and gas extraction. The soot emission factor of 2.6 kg/Mg throughput is taken directly from a

publication relevant to the Mexican oil industry (Villasenor et al., 2003). The NO_x emission factor of 1.4 kg/Mg-gas-burned is the result of a geometric mean of three published values from the Norwegian (Havs, 2012) and Mexican (Villasenor et al., 2003) petroleum industries, and the E&P Forum (Shah and Pope, 1994).

The UK National Atmospheric Emissions Inventory (NAEI) publishes regular updates to a variety of emission factors with the latest published data for the year 2012 (NAEI, 2012). Emission factors are given for both upstream oil production flaring and upstream gas production activities. PM_{10} (particulate matter less than 10 microns in size) and $\text{PM}_{2.5}$ (less than 2.5 microns in size) emission factors of 0.7 and 0.31×10^{-6} kt/t are specified. A NO_x emission factor of 1.4×10^{-6} kt/t is also provided. The emission factors for PM and NO_x are listed for both upstream oil and upstream gas production separately with the same numbers used for each activity. The primary source of these factors is not readily apparent.

The work of Villasenor et al. (2003) is the basis for emission factors applied to the petroleum exploration and production industry in Mexico. The factors reported are broadly referenced from the USEPA AP 42 report and the ARPEL emissions inventory discussed previously. The emission factors of 2.1 g $\text{PM}_{10}/\text{Sm}^3$ and 1.6 g NO_x/Sm^3 match exactly with the sour gas flaring emission factors provided by ARPEL, which is likely the primary source for the emission factors in this work.

As summarized in Table 1.1 and Table 1.2, soot and NO_x emission factors are available from many sources with somewhat limited information as to the source of the emission factor or the applicability to upstream oil and gas flares. The emission factors

as reported are defined using various base units, which underscores the lack of consistency or knowledge on the appropriate scaling of emission factors for different flare gases with a potentially wide range of densities and heating values. Available soot emission factors appear in almost equal number on a mass of soot per mass of flare gas basis and mass of soot per volume of flare gas basis with a single factor given on a mass of soot per energy content of flare gas basis. These emission factors when converted to common units range by more than an order of magnitude from 0.00031 to 0.0034 kg-soot/kg-flare-gas. NO_x emission factors are presented on mass of NO_x per mass, volume, and energy content of flare gas basis. When converted to common units the emission factors range from 0.000533 to 0.00317 kg- NO_2 /kg-flare-gas. The order of magnitude differences among the soot and NO_x emission factors taken from data on flare gases as chemically disparate as methane and crude propylene emphasises the need for caution when using current single-value emission factors and the importance flare gas composition in determining pollutant emission rates. Additionally, it is noted that many of the emission factors are directly referenced or adapted from other emission factors. Specifically, for soot emission the emission factors of ARPEL, CAPP, EEA and Villasenor all come from previously published US EPA factors, which themselves are either taken from confidential test data or the work of McDaniel on crude propylene flames with soot concentration data for an unknown dilution of products. Although current NO_x emission factors are attributed to a more diverse set of sources, details of the test conditions and measurements that produced the factors are limited.

Table 1.1 - Summary of soot emission factors

Standard	Reported Emission Factor	EF Equivalent (kg-PM/kg-flare-gas)	Flare Gas	Primary Source
AP 42, Vol I, Sec 2.4 US EPA (1998)	17 lb/10 ⁶ DSCF Methane	0.00032 ^a	Methane	• Enclosed Flares
AP 42, Vol I, Sec 13.5 US EPA (1995)	0, 40, 177, 274 µg/L exhaust gas ^b	0, 0.00050, 0.00219, 0.00340	Crude Propylene	• McDaniel (1983)
WebFIRE, US EPA (2014)	53 lb/10 ⁶ SCF	0.0010 ^a	Landfill Gas	• Confidential Report No. ERC-55, April 21, 1991
ARPEL (Franklin and Leahey, 1998)	0.0023, 0.0021 kg/m ³ -gas-burned ^c , 43.0 tonnes/PJ-fired	0.0027 ^a , 0.0025 ^a , 0.00228 ^{a,d}	Solution Gas (Sweet, Sour), Natural Gas Steam Assisted	• USEPA External Combustion Sources, 4/93, Table 1.3-10, <i>New Source Performance Standards for Fossil Fuel Fired Burners</i>
CAPP (2007)	2.5632 kg/10 ³ m ³	0.00302 ^a	Solution Gas	• USEPA WebFIRE 6.22, April 21, 1991. Landfill gas adjusted to 45 MJ/m ³ HHV
EEA (Trozzi, 2013)	2.6 kg/Mg-throughput	0.0026	Flaring in Oil and Gas Extraction	• Villasenor et al. (2003)
NAEI (2012)	0.7 ^e , 0.31 ^f x10 ⁻⁶ kt/t	0.0007, 0.00031	Upstream Gas Production	• Unknown
Villasenor et al. (2003)	2.1 g/Sm ³	0.0025 ^a	Sour Gas	• US EPA AP 42 (2001)/ARPEL (1998)

^a Assumed gas density of 0.85 kg/m³

^b Calculated following McEwen (2010), corrections made for crude propylene

^c Values given are for “Solution Gas Combustion Heavy Crude Oil Primary (Sweet)/Thermal (Sour) Facilities” respectively

^d Assumed HHV of 45 MJ/m³

^e PM₁₀

^f PM_{2.5}

Table 1.2 - Summary of NO_x emission factors

Standard	Reported Emission Factor	EF Equivalent (kg-NO _x /kg-flare-gas)	Flare Gas	Primary Source
AP 42, Vol I, Sec 2.4 US EPA (1998)	40 lb/10 ⁶ DSCF Methane	0.00075 ^a	Methane	<ul style="list-style-type: none"> Enclosed Flares
AP 42, Vol I, Sec 13.5 US EPA (1995)	0.068 lb/10 ⁶ BTU	0.0014 ^{b,c}	Crude Propylene	<ul style="list-style-type: none"> McDaniel (1983)
WebFIRE, US EPA (2014)	28.3 lb/10 ⁶ SCF	0.000533 ^a	Landfill Gas	<ul style="list-style-type: none"> Confidential Report No. ERC-55, April 21, 1991
ARPEL (Franklin and Leahey, 1998)	0.0016 kg/m ³ -gas ^d , 59.9 tonnes/PJ-fired	0.0019 ^a , 0.00317 ^{a,e}	Solution Gas (Sweet, Sour), Natural Gas Steam Assisted	<ul style="list-style-type: none"> CAPP, <i>Climate Change Workshop on Benchmarking of Energy Use and Emissions</i>, Calgary, Alberta, July 18, 1995 CAPP Guide: Voluntary Challenge, June 30, 1995, Table 3
CAPP (2007)	1.345 kg/10 ³ m ³	0.001582 ^a	Solution Gas	<ul style="list-style-type: none"> USEPA AP 42 1995, Section 13.5 adjusted to 45 MJ/m³ HHV
E&P Forum (Shah and Pope, 1994)	0.0015 tonnes/tonne-flared	0.0015	Solution Gas	<ul style="list-style-type: none"> OLF (1991), UKOA (1993), Internal Data
EEA (Trozzi, 2013)	1.4 kg/Mg-gas-burned	0.0014	Flaring in Oil and Gas Extraction	<ul style="list-style-type: none"> OLF (2012), Villasenor et al. (2003), E&P Forum (1994)
NAEI (2012)	1.4x10 ⁻⁶ kt/t	0.0014	Upstream Gas Production	<ul style="list-style-type: none"> Unknown
Villasenor et al. (2003)	1.6 g/Sm ³	0.0019 ^b	Sour Gas	<ul style="list-style-type: none"> US EPA AP 42 (2001)/ARPEL (1998)

^a Assumed gas density of 0.85 kg/m³

^b Assumed gas density of 1.90 kg/m³

^c Assumed HHV of 93 MJ/m³

^d Value given is for Solution Gas Combustion Heavy Crude Oil Primary (Sweet)/Thermal (Sour) Facilities

^e Assumed HHV of 45 MJ/m³

1.3 Flow Regimes for Non-premixed Diffusion Flames and Flares

Efforts have been made (Delichatsios, 1993) to distinguish flames into a number of regimes through various dimensionless expressions which speak to the overall fluid dynamic characteristics of the flame itself. These efforts deconstruct the flame into two regions: a transition region close to the nozzle and the remainder of the flame downstream of this region. Flames can exist in which both regions are laminar, both regions are turbulent, or the transition region is laminar while the rest of the flame is turbulent. As proposed by Delichatsios (1993), in cases where the Reynolds number exceeds 4000, turbulence is induced by inertia (momentum) in the region near the exit of the nozzle. Alternatively at Reynolds numbers lower than 4000, transition from a laminar flame at the nozzle exit and laminar conditions in the nozzle exit to turbulent conditions in the downstream region can occur through buoyancy mechanisms caused by combustion related density gradients. Delichatsios (1993) suggests that a dimensionless Froude number, which compares gravitational and inertial properties, can be useful to describe which regime describes a given flame as illustrated in Figure 1.2. Several modifications to the basic Froude number are suggested which take into account stoichiometric and other fuel chemistry effects. Reynolds number (Re) and the modified Froude number known as the Global Froude number (Fr_g) are defined by Eq. (1.1) and Eq. (1.2) below. An additional parameter, the Fire Froude number (Fr_f), which will be discussed later in Chapter 4 is defined by Eq. (1.3).

$$Re = \frac{\rho_0 u_0 d_0}{\mu_0} \quad (1.1)$$

$$Fr_g = \frac{u_0 f_s^{3/2}}{(g d_0)^{1/2}} \left(\frac{\rho_\infty}{\rho_0} \right)^{1/4} \quad (1.2)$$

$$Fr_f = \frac{u_0 f_s^{3/2}}{(g d_0)^{1/2}} \left(\frac{\rho_\infty}{\rho_0} \right)^{1/4} \left(\frac{T_\infty}{\Delta T_f} \right)^{1/2} \quad (1.3)$$

In Eq. (1.1) above, ρ is the density, u is the velocity, d is the diameter, and μ is the viscosity, where subscript 0 represents conditions at the exit of the flare. In addition, for Eq. (1.2) and Eq. (1.3), f_s is the stoichiometric mixture fraction, g is the gravitational constant, and T is the temperature, where subscript ∞ represents ambient conditions and ΔT_f is calculated as T_∞ subtracted from the adiabatic flame temperature, T_{ad} .

Figure 1.2: Delichatsios (1993) map showing regimes for jet diffusion flame exit conditions defined by exit Reynolds number and Global Froude number as defined by Eq. (1.2).

Recent work (Costa et al., 2004) suggests the transition from buoyancy to momentum dominated flames may also be important when investigating NO_x emissions as shown in Figure 1.3. Experiments expanding earlier work (Rokke et al., 1992), which investigated primarily buoyancy controlled flames, to include flames in the momentum controlled regime suggest there may be a decrease in the defined NO_x emission index at

increased Froude numbers (Fr) as defined by Eq. (1.4). The same experiments show a decline in radiant fraction of the flame in the buoyant region before a possible leveling off of radiant fraction in the momentum dominated flames. However no correlation was found between the measured radiant fraction and a NO_x emission index. This suggests any dependence of NO_x emission index on radiant fraction is secondary to the effects accounted for in the Froude number correlation ($Fr^{3/5}$).

$$Fr = \frac{u_0^2}{gd_0} \quad (1.4)$$

Figure 1.3: Costa et al. (2004) figure showing NO_x emission index scaling changes for jet diffusion flames transitioning from buoyancy-dominated to momentum-dominated regimes as characterized by the exit Froude number as defined by Eq. (1.4).

The preceding definitions of flame regimes and their suspected impact on emissions over a wide range of operating conditions is developed considering only the nozzle outlet conditions for vertical diffusion flames. In real world gas flaring

applications, flames are subject to varying speeds of crosswind which will also have an effect on the combustion process. Primarily, transitions between laminar and turbulent flow at the outlet of the nozzle are complicated by the increased mixing via the presence of these crosswinds. Work on this subject has shown the importance of both the relative jet and crossflow velocities using a “mixing index” (product of air and fuel velocities) (Ellzey et al., 1990) and momentum ratio (ratio of fuel and crossflow velocities squared) (Bandaru and Turns, 2000; Johnson and Kostik, 2000). The quantifiable impact of crosswind on soot emissions, NO_x emissions, and combustion efficiency is discussed further in Sections 1.4.1, 1.4.2, and 1.4.3 respectively.

1.4 Existing Literature on Emission Quantification from Turbulent Non-Premixed Diffusion Flames

1.4.1 Soot Emissions Measurements

Becker and Liang (1982) examined free turbulent diffusion flames for a range of alkane and alkene fuels measuring soot emissions and radiant cooling (ratio of radiant heat loss and energy of combustion). Both were found to plateau at a Richardson number, Ri , (defined in Eq. (1.5)), with L_f denoting the flame length) greater than 2000. Soot emissions expressed as a “soot yield factor” (ratio of soot output to carbon input) were observed to plateau at 0.0015-0.0045 for fuels other than acetylene, which had ~ 100 times greater soot yields. The soot yield factor stabilized at ~ 0.0003 for Richardson numbers less than 200, where buoyancy was found to be unimportant. The experimental results and the form of the Richardson number, with its inverse proportionality to exit velocity, indicate that soot emissions are up to an order of magnitude greater at low velocities compared to high velocities for a given flare gas.

$$Ri = \frac{gL_f^3}{(u_0 d_0)^2} \left(\frac{\rho_\infty}{\rho_0} \right) \quad (1.5)$$

Sivathanu and Faeth (1990) measured the overfire soot volume fractions on 5, 50 and 234 mm burners for acetylene, propylene, ethylene, and propane buoyant jet-flames. Soot generation (percent of fuel carbon converted to soot) was found to vary with residence time before plateauing for residence times much larger than the smoke point residence time.

McEwen (2010) measured soot yields from lab-scale flares burning methane and methane-based flare gases from 12.7 to 76.2 mm. Based on the results it was suggested that soot yield may plateau for burners over 38.1 mm in diameter operating at conditions where the Fire Froude number is greater than 0.003. Comparisons to emission factors were made and the potential soot yield scaling with the gas heating value was made for heating values in the range of 38 to 47 MJ/m³. The suggestion of soot yield plateauing at increased Froude numbers contradicted the relation Becker and Liang (1982) found between soot yield and the Richardson number.

There are significantly less data available on the effect of crosswind on soot or BC emission rates. Ellzey et al. (1990) studied the soot yield from small diameter (1.19 to 2.41 mm) propane diffusion flames in cross-flow and co-flow configurations. They showed that soot yields decreased with the scaled product of jet and air velocities for the cross-flow configuration. The reduction in soot yield with increases of air velocity was attributed to higher mixing. The effect of crosswind on BC emissions is an obvious area

for future work, however the goals of the present work are to examine the zero-crosswind condition in which soot yield is may be at a maximum.

Table 1.3 - Summary of literature reporting soot emissions from turbulent non-premixed diffusion flames

Reference	Diameter(s) (mm)	Velocities (m/s)	Fuel	Flame Type	Goals and Conclusions and Notes
(Becker and Liang, 1982)	0.7 – 10.9	8 – 170	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , C ₂ H ₄ , C ₂ H ₂	Turbulent buoyant flames ranging from forced to fully natural convection	<ul style="list-style-type: none"> C₂H₄ > C₃H₈ > CH₄, C₂H₆ soot emission
(Sivathanu and Faeth, 1990)	5 – 234	< 30	C ₂ H ₂ , C ₂ H ₄ , C ₃ H ₆ , C ₃ H ₈	Diffusion flames in still air	<ul style="list-style-type: none"> Soot generation on per fuel basis increased with flame residence time before approaching asymptotes SVF directly related to mixing and analogous to laminar flamelet concept for nonpremixed flames
(McEwen and Johnson, 2012)	12.7 – 76.2	0.1 – 2.2	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , C ₄ H ₁₀	Diffusion flame with N ₂ and CO ₂ diluent	<ul style="list-style-type: none"> Soot yields possibly plateau at Fire Froude numbers greater than 0.003 Potential for scaling with flare gas heating value proposed
(Ellzey et al., 1990)	1.19 – 2.41	0.351 – 1.981	C ₃ H ₈	Diffusion flame in cross- flow and co-flow	<ul style="list-style-type: none"> Soot yield decreases with scaled product of jet and air velocity in cross-flow Diameter not an important parameter
(McDaniel, 1983)	101.6 / 219.075	0.03 – 8.7	Crude Propylene	Air- and steam-assisted industrial flares	<ul style="list-style-type: none"> Four undiluted soot concentrations measured for heavy-, average-, light- and non-smoking operating conditions with varying steam-assist
(Pohl et al., 1986)	76.2 – 304.8	< 300	C ₃ H ₈	Steam-assisted flare with N ₂ diluent	<ul style="list-style-type: none"> Soot accounts for less than 0.5% of emitted carbon
(Allen and Torres, 2011)	609.6 / 914.4	0.083 – 0.24	C ₃ H ₆ , C ₃ H ₈ , natural gas	Air- and steam-assisted industrial flares	<ul style="list-style-type: none"> Soot emissions less than 0.5% of the fuel carbon on a molar basis

1.4.2 NO_x Emissions Measurements and Suggested Scaling

Several investigations have been made throughout the literature examining the emissions of NO_x from turbulent non-premixed diffusion flames and the potential for emissions scaling of NO_x. Experiments on propane flames (exit velocities, u_0 , of 2.2 – 240 m/s and stack diameters, d_0 , of 4 – 50 mm) and methane flames ($u_0 = 9.5 – 81$ m/s, $d_0 = 10 – 28$ mm) were performed (Rokke et al., 1992) and compared with previous literature and a theoretical scaling expression (proposed by Rokke) as part of an investigation into the emissions of NO_x over a range of Froude numbers in the buoyancy-controlled flame regime. Using a simple tube burner with no pilot, measurements of the relevant gases were measured in axial- and radial-profiles using a moveable single point probe. The measured ratio of NO_x to CO₂ was used to calculate a NO_x emission rate or yield. In a comparison with literature available at the time of Rokke et al. (1992), the proposed scaling relation (Eq. (1.6)) appears to fit the data well for the various hydrocarbons and non-hydrocarbon fuels as shown in Figure 1.4. The theoretical scaling law in which flame volume is the most important parameter was derived from chemical kinetics and jet flame behaviour and examines three mechanisms for NO_x production: the thermal, prompt, and nitrous-oxide mechanisms (Rokke et al., 1992).

$$E_{NO_x} \left[\frac{\rho_0 u_0}{d_0} \right] \left(\frac{g}{m^3 s} \right) \approx 44 Fr^{0.6} \quad (1.6)$$

Figure 1.4: Proposed NO_x scaling law including experimental data from literature (Rokke et al. 1992). Froude number is defined by Eq. (1.4).

More recent work (Costa et al., 2004) looked to re-examine NO_x emissions and scaling in the buoyancy dominated regime and extend understanding into the momentum dominated regime. Methane flames were tested on 5, 6 and 8 mm burners with exit velocities ranging from 9.4 – 89.9 m/s. The measurements suggest transition from buoyancy- to momentum-controlled flames occurs at a Froude number of approximately 10,000, with scaling in the buoyancy-controlled region agreeing well with the proposed scaling law of Eq. (1.6). In the momentum-controlled region, the data suggest the NO_x

emission index dependency decreases to $Fr^{0.35}$. NO_x emissions were examined in the context of measurements on flame geometry and radiant fractions.

Propane and ethylene flames (Santos and Costa, 2005) were subsequently tested as an extension of the previously discussed methane experiments. Using the same three burners (5, 6 and 8 mm), exit velocities of 5 - 137.4 m/s were tested to span the buoyancy- and momentum-controlled regime transition. It was found that the transition point varies depending on the hydrocarbon fuel tested with the data suggesting that it is the sooting propensity and related flame radiation losses and not the flame regime that may control the NO_x scaling. Additionally, data from sooty (ethylene) flames suggest a unique scaling parameter compared to earlier data.

The first comprehensive NO_x emissions study of flames in cross-flow (Bandaru and Turns, 2000) utilized a 4.12 mm horizontal tube with jet velocities of 15 – 100 m/s burning in a vertical air jet. Pure methane, propane and ethylene were burned over a wide range of jet velocities in one or two different cross-flow conditions. Pilot flames were used in some instances to maintain a minimum allowed flame attachment with the burner tube. The results show that NO_x yield on a mass per mass of gas flared basis remains relatively flat regardless of fuel jet velocity. The propane and ethylene flames exhibited higher NO_x emissions at higher cross-flow velocities while the methane was tested only at a single cross-flow velocity. It is suggested that a decrease in radiant fraction and therefore soot production caused by the strong cross-flow creates a hotter flame and increased NO_x production in the ethylene flame.

The author is not aware of any comprehensive examination of the effect of horizontal crosswind on NO_x production from a vertical diffusion flame (as relevant to a gas flare) with the possible exception of one recent paper using a pilot-scale flame with an open fan system (Talebi et al., 2014). A burning methane/propane/butane mixture was subjected to cross-flow from the open-fan system and single-point sampling was used to estimate emission indices. The results suggest NO_x may decrease slightly (approximately 30% for range of cross-flow tested) with crosswind. Similar to the examination of soot yield in the current work, it is expected that the results for NO_x yield under quiescent conditions will represent a maximum.

Table 1.4: Summary of literature reporting NO_x emissions from turbulent non-premixed diffusion flames

Reference	Diameter(s) (mm)	Velocities (m/s)	Fuel(s)	Flame Type	Goals and Conclusions and Notes
(Rokke et al., 1992)	4 – 50	2.2 – 240	CH ₄ , C ₃ H ₈	Unconfined, vertical, turbulent jet diffusion flame	<ul style="list-style-type: none"> • Good agreement between experimental results and scaling theory
(Costa et al., 2004)	5 – 8	9.4 – 89.9	CH ₄	Unconfined, vertical, turbulent jet diffusion flame	<ul style="list-style-type: none"> • Transition from buoyancy to momentum driven occurs at $Fr = 10^4$ • For buoyancy dominated flames volume is the primary scaling factor
(Santos and Costa, 2005)	5 – 8	5 – 137.4	C ₃ H ₈ , C ₂ H ₂	Unconfined, vertical, turbulent jet diffusion flame	<ul style="list-style-type: none"> • Soot propensity and not flame regime is critical for establishing NO_x scaling • New NO_x correlation proposed for sooty flames
(Bandaru and Turns, 2000)	4.12	15 - 100	CH ₄ , C ₃ H ₈ , C ₂ H ₄	Horizontal diffusion flame in cross-flow	<ul style="list-style-type: none"> • Higher NO_x yield in ethylene than other flames (g/kg) • NO_x yield coupled to soot by radiant fraction
(Talebi et al., 2014)	unknown	unknown	CH ₄ , C ₃ H ₈ , C ₄ H ₁₀	Diffusion flame in cross-flow	<ul style="list-style-type: none"> • NO_x yield decreases with increasing crosswind
(McDaniel, 1983)	101.6 / 219.075	0.03 – 8.7	Crude Propylene	Air- and steam-assisted industrial flares	<ul style="list-style-type: none"> • 0.018 to 0.208 lb/10⁶ Btu with an average of 0.068 lb/10⁶
(Allen and Torres, 2011)	609.6 / 914.4	0.083 – 0.24	C ₃ H ₆ , C ₃ H ₈ , natural gas	Air- and steam-assisted industrial flares	<ul style="list-style-type: none"> • 0.009-0.033 lb NO_x/10⁶ BTU for steam-assisted flaring • 0.037-0.083 lb NO_x/10⁶ BTU for air-assisted flaring

1.4.3 Studies of Combustion Efficiency

Measurement of combustion efficiency (generally the percent of fuel carbon oxidized to form CO_2) of lab-scale flames in the literature is quite limited. Stroscher (2000) conducted measurements on lab-, pilot- and field-scale flares to measure combustion efficiencies and hydrocarbon emissions. Lab-scale tests included flows of pure flare gases, hydrocarbon liquids and entrained mixtures on flares with tip orifice diameters of 0.1-3.0 mm and a maximum exit velocity of Mach 0.2. Pilot-scale experiments extended the range of diameters tested to 2-6 mm. Results of lab and pilot scale tests showed flares burning methane to have combustion rates greater than 99%, while flares burning propane produced elevated soot compared to the methane flames and had combustion efficiencies around 98%. Field tests in which samples were extracted from a single point probes suspended downstream of the flame tip were conducted on sweet gas flares at an oil battery and sour gas flares at a different battery. Local efficiencies at the probe as low as ~62% were reported. Addition of liquid fuels to the flare gas stream, the presence of crosswind and impurities in the flare gases at the field sites were suggested as reasons for the low efficiency values.

The effect of cross-flow on combustion efficiency (Kostiuk et al., 2000) has been studied in some detail, where wind tunnel experiments suggest that efficiencies remain relatively high (greater than 96.5%) unless the flame is subjected to a strong crosswind (greater than 6 m/s) (Johnson and Kostiuk, 2000) or low flare gas heating value (equal to or less than 20 MJ/m^3) (Johnson and Kostiuk, 2002). It is suggested that the decrease in combustion efficiency at cross winds is a results of unburned fuel ejected near the exit of the stack (Poudenx, 2000; Johnson, Wilson, et al., 2001). Efficiency measurements at

zero-crosswind as in the present experiments therefore represent a best case scenario for the conversion of hydrocarbon to carbon dioxide at high combustion efficiency. A discussion of additional combustion efficiency measurements conducted on large-scale flares is continued in Section 1.5.

Table 1.5: Summary of literature reporting combustion efficiency from turbulent non-premixed diffusion flames

Reference	Diameter(s) (mm)	Velocities (m/s)	Fuel	Flame Type	Goals and Conclusions and Notes
Stroscher (2000)	0.1 – 200	< Mach 0.2	CH ₄ , C ₃ H ₈ , liquid fuels, natural gas, solution gas	Non-premixed diffusion flame	<ul style="list-style-type: none"> Efficiencies > 99% for CH₄ flames for laminar, transitional and turbulent flows Efficiencies ~ 98% for C₃H₈ flames with increased soot Pilot- and field-scale flares showed decreased efficiencies partially due to flare gas contents and crosswinds
Kostiuk et al. (2000)	10.8 – 33.3	0.5 – 2.0	Natural gas, propane	Non-premixed diffusion flame in crosswind	<ul style="list-style-type: none"> High efficiencies (> 99.5%) for flames in near-quiescent conditions Decrease in efficiency down to ~88% with increasing crosswind
Johnson and Kostiuk (2000)	24.6	1.0 – 4.0	Natural gas, propane	Non-premixed diffusion flame in crosswind	<ul style="list-style-type: none"> Increased cross wind speed lowers combustion efficiency Increased jet velocity lessens the effects of crosswind
McDaniel (1983)	101.6 / 219.1	0.03 – 8.7	Crude Propylene	Air- and steam-assisted industrial flares	<ul style="list-style-type: none"> Efficiency calculated from single point samples collected above a vertical flare with high efficiencies found except when detached
Pohl et al. (1986)	76.2 – 304.8	< 300	C ₃ H ₈	Steam-assisted flare with N ₂ diluent	<ul style="list-style-type: none"> Efficiencies high (> 98%) when flame is stable
Allen and Torres (2011)	609.6 / 914.4	0.083 – 0.24	C ₃ H ₆ , C ₃ H ₈ , natural gas	Air- and steam-assisted industrial flares	<ul style="list-style-type: none"> High efficiencies until steam-quenched

1.5 Field Measurements of Large-Scale Flares

The measurement of gas and solid phase emissions from in-situ flares remains a difficult task. To date a limited amount of work exists in which experimental measurements of flares have progressed beyond lab-scale. The work of McDaniel (1983) is one of the first instances of this scale of work being accomplished, although measurements of BC were presented in terms of plume concentrations only. Performed on both air- and steam-assisted flares burning crude propylene (80% propylene and 20% propane by volume), and primarily investigating combustion efficiency, this work provided the basis for many US EPA emission factors as detailed previously. Steam-assisted flare tests were performed on a 219.1 mm diameter industrial flare with an outlet area of 27.0 in² and crude propylene flow rates of 24.4 – 473 SCFM and varying steam-assist rates. Air-assisted flaring was performed on a 101.6 mm diameter industrial flare with one of two “spider” burners having outlet areas of 5.30 or 11.24 in² and crude propylene flow rates of 22.7 – 481.6 SCFM and varying air-assist rates. Additional tests were performed on both flares in which the crude propylene was diluted with nitrogen to produce a lower energy content flare gas. Flow rates with nitrogen dilution were expanded to 0.35 – 703 SCF per minute and 0.54 – 639 SCF per minute for steam- and air-assisted flaring respectively. Results from the testing campaign suggest that combustion efficiency was generally high (> 98%) with a small decrease for highly diluted relief gas and large decreases when excessive steam- or air-assist was employed. Soot emissions were recorded for three individual tests in which no steam- or air assist was employed and the relief gas was not diluted. Soot emissions were measured as a concentration and resulted in 40, 177 and 274 µg/L with the non-smoking tests assumed zero. NO_x emissions varied

widely over conditions including steam- and air-assist and varying levels of relief gas dilution (from 0.018 to 0.208 lb/10⁶ Btu) with an average of 0.0672 lb/10⁶ Btu and standard deviation of 0.0393 lb/10⁶ Btu.

Combustion efficiency and soot emission measurements were later made on flares ranging from 3 – 12 inches burning propane (Pohl et al., 1986). While soot emissions were not measured directly as either a rate or yield, they are stated to account for less than 0.5% of the unburned hydrocarbons emitted. The study showed that combustion efficiency remains high (> 98%) up to the point of stability (dependent on either exit velocity or a decreased heating value).

Recent work by the University of Texas through the Texas Commission on Environmental Quality (TCEQ) reported measurements on a pair of industrial flares associated with air- and steam-assisted flaring (Allen and Torres, 2011). The primary scope of the study was to investigate combustion efficiency and hydrocarbon destruction removal efficiency. The gases flared consisted of pure propylene as well as propylene/natural gas and propane/natural gas mixtures. Dilution of the hydrocarbon mixture with nitrogen allowed for varied energy content gas to be flared. Additionally, NO_x emissions were reported for a limited number of test cases burning propane/natural gas mixtures (Torres, Herndon, Wood, et al., 2012) and ranged from 0.009-0.033 lb NO_x/10⁶ Btu for steam-assisted flaring and 0.037-0.083 lb NO_x/10⁶ Btu for air-assisted flaring. Carbon particulate emissions were mentioned only in passing and were suggested to constitute less than 0.5% of the fuel carbon on a molar basis (Torres, Herndon, Kodesh, et al., 2012) or approach 0.2% of the total carbon by mole at the highest soot emitting conditions (Herndon et al., 2012).

Measurements of NO_x emissions from large onshore flares in Norway were conducted (Bakken et al., 2008) at four separate installations using Differential Absorption Lidar (DIAL). The data released with industry cooperation are averages of both NO_x and flare gas flow rates over the measurement period. Flaring was generally performed at low and constant rates on 0.55 – 1.22 metre diameter burners with flare gas composition including both methane and hydrogen with possible steam-assist. Heating values of the flared gas also varied with the inclusion of diluents in the gas stream.

More recently, a technique for quantifying in situ BC mass emission rates from flares known as sky-LOSA has been deployed in field measurements (Johnson et al., 2013; Johnson et al., 2011; Johnson et al., 2010). In these limited field trials, flares have been found to emit BC at rates varying from 0.067 g/s to 2.0 g/s, although to date these measurements have not been referenced to known flare gas flow rates or flare gas composition.

1.6 Thesis Motivation & Objectives

The motivations for the current work stem from the questionable applicability of current single value emission factors for soot and NO_x as well as the critical lack of data at the operating conditions of upstream oil and gas flares as characterized by low Froude numbers ($< \sim 100$ as defined by Eq. (1.4), $< \sim 0.1$ as defined by Eq. (1.2)). The lack of quantitative data with defined uncertainties in the range of operating conditions examined in the current work is important for qualifying the effects of operating regimes on the emissions of turbulent non-premixed diffusion flames. The critical lack of data available in literature to allow for accurate quantification of soot emissions from buoyancy-

dominated flames is a compelling reason for the continuation of research on the subject (Crosland et al., 2014).

As such, the objectives for the current work were as follows:

- Construct and commission the Carleton Lab-Scale Flare facility and develop a quantitative methodology for evaluating flare performance in terms of overall combustion efficiency and various species emission rates with associated uncertainties;
- Develop a methodology for evaluating combustion efficiency and species emissions from a non-premixed diffusion flame which does not require explicit measurement of the plume flow rate;
- Develop an ancillary method for injecting a tracer gas into the plume upstream of the combustion zone such that direct measurement of the plume flow rate can be made (where the two distinct measurement methods will present distinct uncertainties and have inherent advantages to application in different scenarios);
- Generate new data to confirm the expected high combustion efficiencies as well as quantify BC, NO_x and other emission rates for turbulent, non-premixed diffusion flames operating in the buoyancy-dominated regimes typical of upstream oil and gas flaring;
- Investigate the trends discernable in combustion efficiency and various species emission rates as burner diameter, exit velocity, and flare gas composition are varied; and

- Investigate the potential for correlating results to facilitate the development of improved BC and NO_x emission factors for flares relevant to the upstream oil and gas industry.

1.7 Overview of Thesis

Chapter 2 details the experimental setup used in the current work. Chapter 3 reports the development of a new quantitative methodology and expressions for experimental uncertainty recently published in *Industrial & Engineering Chemistry Research*. Experimental results and discussion are presented in Chapter 4, followed by conclusions and recommendations for further work in Chapter 5.

Chapter 2

Experimental Setup

The Carleton lab-scale flare facility was designed and built to increase the experimental scale of the work accomplished by Canteenwalla (2007) and McEwen (2010) using a smaller-scale experiment housed at the National Research Council of Canada. Specifically, it was desired to create a facility that could accommodate flames up to approximately 3 metres in length at flare gas flow rates of up to 600 standard litres per minute (SLPM). The description of the facility will be discussed in terms of several distinct components, which were either borrowed from previous experiments or designed and built as part of the new facility. These components include: the modular turbulent diffusion burner, the fuel delivery system, the various flare gas compositions tested, the controllable exhaust system, the experimental analysis instrumentation, and the flame imaging equipment. The turbulent diffusion burner was previously used in the work of Canteenwalla (2007) and McEwen (2010) and will be discussed within that context in Section 2.1. Section 2.2 discusses the fuel delivery system and provides details of all components upstream of the burner including the mass flow controllers, gas storage and handling, and other related components. As detailed in Section 2.3, the flare gas compositions examined in the current work were either a selection of pure fuels or a set of mixtures representative of flared gases from the Alberta upstream oil and gas industry. The description of the exhaust system in Section 2.4 includes details of the exhaust

system design, as well as the physical dimensions of the exhaust collection system and the immediate surroundings of the burner. Section 2.5 discusses the gaseous species and soot sampling equipment as well as details of the temperature and pressure sensors. Section 2.6 describes the flame imaging equipment and includes details of the camera and associated hardware as well as a discussion of the imaging procedure.

Figure 2.1: Experiment schematic with flare pit dimensions and overview of fuel delivery system, air supply system, hood and screen details, and dilution tunnel overview.

2.1 Turbulent Diffusion Burner

Designed by Canteenwalla (2007), the modular burner includes five different tip sizes, of which three were used in the current work (38.1, 50.8 and 76.2 mm internal diameter (ID)). Briefly, the flare gas is delivered to the burner by tubing that is further discussed in Section 2.2. The upstream tubing runs along the floor of the flare pit and connects to the burner with a 90° elbow which enters the burner vertically from

underneath as shown at the bottom of Figure 2.2. The flare gas passes through a diffusion chamber filled with 5 mm diameter glass beads that diffuse the incoming fuel jet before it enters a vertical constant diameter settling chamber containing three evenly spaced mesh screens. The diffuser and settling chamber are shared between all burner diameters. The topmost three components as shown in Figure 2.2 (converging nozzle, turbulence generating grid and burner exit) are interchangeable as a set, with each burner exit section having a dedicated turbulent generating grid and converging nozzle tailored to the dimensions of the given exit tube.

The burner exit tubes were designed and manufactured with an inner to outer diameter ratio of 0.89, which is representative of simple pipe flares. Exit length and turbulence generating grids were designed to produce fully developed turbulent pipe flow at the exit plane characteristic of real flares. Details on the velocity profile, and turbulence intensity ($\sim 3 - 6\%$ at the core) at the exit plane for the 38.1 mm burner as well as overall burner dimensions can be found in the work of Canteenwalla (2007).

Figure 2.2: Modular burner schematic (Canteenwalla, 2007).

The temperature of the flare gas in the burner exit was measured using a 1/16" diameter K-type thermocouple probe (CASS-116G-12) which passed approximately 5 mm over the top edge of the burner and was bent 90° extending upstream into the burner exit 45 mm.

2.2 Fuel Delivery System

The fuel delivery system is comprised of six independently-controlled Brooks mass flow controllers (MFC), which control the flow of various pure gases contained in pressurized cylinders. The controllers were operated using either analog (a) or digital (d) communications and included Smart Series controllers 5853S(d) for methane (0 – 600 SLPM), SLA5851S(a) for ethane (0 – 50 SLPM), SLA5851S(d) for propane (0 – 25 SLPM), SLA5851S(a) for butane (0 – 10 SLPM), SLA5851S(a) for carbon dioxide (0 –

20 SLPM), and 5850S(d) for nitrogen (0 – 16 SLPM). Standard conditions are defined as a pressure of 1 atmosphere (101.325 kPa) and a temperature of 273.15 K.

For the specified gases, calibration of the flow controllers was accomplished using either a SENSIDYNE Gilibrator 2 (0 – 30 litres per minute) or a Siemens Sitrans F C Mass 2100 Coriolis flowmeter. Additionally, for cases where either pure ethylene or propane was flared, the 5853S(d) methane controller was used to allow flow rates of up to 182.41 and 109.45 SLPM respectively. In these instances the Coriolis meter was installed upstream of the Brooks MFC to directly measure the mass flow of the flare gas during the test.

During the development of the final test protocol it was determined that cooling of the gases due to expansion in the pressurized cylinders and across regulators over the length of the test could be significant enough to affect the ability of the Brooks MFC to provide a steady flow rate. As such, a heated water bath was installed upstream of the mass flow controllers and each gas was passed through 25 feet of 1/2" or 1/4" diameter coiled copper tubing immersed in the bath. Tests were operated with the bath at a constant temperature of 25°C with heating and temperature control provided by a Thermo Scientific SC 150 Immersion Circulator. T-type grounded-thermocouples (Omega TC-T-NPT-G-72) were installed downstream of the bath and upstream of the MFCs to ensure a steady gas temperature was held for the duration of each flare test. Downstream of the MFCs, the pure gases were combined and mixed in a 60 cm long, 50.8 mm diameter mixing chamber, after which approximately 12 metres of 3/4" steel tubing lead to the modular burner stand.

2.3 Flare Gas Compositions

Five flare gas compositions were chosen for the current work based on their relevance to upstream oil and gas flaring. The two methane-based flare gases are representative of compositions relevant to the Alberta upstream oil and gas industry as detailed in the work of McEwen (2010) and based on industry correspondence. Three pure flare gases including methane, ethylene, and propane were tested based on their varying propensity to soot and respective relevance to industrial flaring applications. The flare gas compositions and details on gas purity can be found in Table 2.1 below.

Table 2.1: Flare Gas Mixtures Tested

Component Species	Component Purity (%)	Flare Gas Mixture Compositions (by volume)				
		Average 6-Mix (%)	Heavy 4-Mix (%)	Pure CH ₄ (%)	Pure C ₂ H ₄ (%)	Pure C ₃ H ₈ (%)
Methane	99.0	85.24	74.54	100	0	0
Ethane	99.0	7.06	15.47	0	0	0
Propane	99.0	3.11	6.83	0	0	100
n-Butane	99.0	1.44	3.16	0	0	0
CO ₂	99.9	1.91	0	0	0	0
N ₂	99.999	1.24	0	0	0	0
Ethylene	99.5	0	0	0	100	0

Additional information on relevant properties of the mixed and pure flare gases can be found in Table 2.2. All properties are evaluated at standard temperature and pressure (273.15 K and 1 atm). Higher heating values and adiabatic temperatures for the flare gases were obtained from NASA Chemical Equilibrium with Applications (CEA) computer program and evaluated for stoichiometric combustion.

Table 2.2: Flare Gas Properties

Property	Average 6-Mix (%)	Heavy 4-Mix (%)	Methane (%)	Ethylene (%)	Propane (%)
Molecular Weight (kg/kmol)	19.19	21.46	16.04	28.05	44.10
Density (kg/m ³)	0.86	0.96	0.72	1.25	1.97
Higher Heating Value (kJ/kg)	51061	53506	55528	50313	50368
Volumetric Heating Value (kJ/m ³)	43729	51228	39747	62977	99099
Adiabatic Flame Temperature (K)	2228.3	2240.3	2224.2	2264.8	2368.2
Stoichiometric Air-Fuel Ratio	16.33	16.57	17.19	14.75	15.64
Stoichiometric Mixture Fraction	0.059	0.057	0.055	0.064	0.060
Carbon Density (kg-carbon/kg-flare-gas)	0.739	0.776	0.749	0.856	0.817

2.4 Exhaust System and Experimental Infrastructure

The exhaust system and experimental infrastructure for the current work was designed and built to accommodate heat release rates and flame lengths corresponding to the flaring of up to 600 SLPM of methane. A limiting factor in the design process was to maintain an acceptable upper temperature limit in the duct at the highest flow rates of flared gas. Construction of the facility required the installation of a concrete flare pit in a shared laboratory space at Carleton University as seen in Figure 2.1. The pit, measuring 1.88 metres deep, is an irregularly shaped hexagon in which the modular burner is centred. An air supply system was installed at the base of the pit walls to overcome issues related to expected recirculation zones that were encountered during the commissioning process. Perforated plastic pipe was installed around the pit circumference with air supplied by a pair of inline fans installed on opposing pit walls. Supply air was drawn from the end of the laboratory opposite the flare pit through steel ducting. Centered above the modular burner is a custom, steel-constructed hexagonal-

exhaust hood which measures approximately 1.8 metres per side with an included diameter of 3.1 metres. The bottom plane of the hood hangs 3.14 metres above the floor of the pit. The exhaust hood contracts to a 40.6 cm diameter opening which connects to the dilution tunnel. At the far downstream end of the dilution tunnel, an IAP Vane Axial VAX 180 exhaust fan controlled by a 5 HP Danfoss VLT-HVAC variable speed drive provides up to 100,000 SLPM of ventilation. The maximum exhaust flow rate and dimensions of the exhaust hood correspond to a maximum face velocity of 0.22 m/s at the entrance plane of the hood.

The dilution tunnel is constructed from round steel ducting and is wrapped in insulation to limit heat loss from the sample volume and maintain temperature from the hood exit to the sample points. The duct extends vertically from the top of the hood and bends 90° to the horizontal. It follows a diagonal path before bending 45° and running perpendicular to the exit wall. A total horizontal length of 10.6 metres extends from the 90° bend to the sampling location.

The hood suspends two concentric wire mesh shrouds (1.5 and 3.1 metres in diameter) centered on the burner axis and hanging 0.42 and 0.60 metres above the pit floor respectively. The screens are intended to reduce turbulent air flow that may be created by the irregular shape of the pit or its location in the laboratory.

The pressure and temperature of the dilution tunnel were measured at the sample location shown in Figure 2.3. The temperature was measured using a 1/8" diameter T-type thermocouple probe (Omega CPSS-18-G-12) inserted such that the tip was positioned in the centre of the dilution tunnel. The barometric pressure in the lab was

measured with an Omega pressure transducer (part number MMB26V10H2C0T3A8P) capable of measuring 880-1100 mBar. The sample pressure in the dilution tunnel was measured by an Ashcroft CXLdp differential pressure transducer with a range of 2 inches water column. The negative terminal of the differential pressure transducer was connected to a network of flexible nylon tubes which connected to four static pressure taps spaced evenly on the circumference of the dilution tunnel at the sample location. The static taps were constructed of 1/2" male NPT fittings threaded into flat steel plate. The steel were mounted flush to the outside dilution tunnel.

Figure 2.3: Diagram of probe locations in dilution tunnel. LII, FTIR, and thermocouple probe locations and dimensions shown. Pressure tap locations marked.

To accommodate measurement of the dilution tunnel flow rate using an injected tracer gas, an injection point downstream of the combustion zone just inside the dilution tunnel entrance was selected. Labeled as the tracer injection location in Figure 2.1, the tracer gas is delivered to the injection point from a pressurized gas cylinder by a

dedicated Brooks SLAMf50 digitally-controlled mass flow controller with a range of 0-5 SLPM of C_2H_2 . At the injection point, a standard 1/4" stainless steel tube is inserted through the wall of the dilution tunnel. Connected to the internal end of the tube is a 10" diameter ring constructed of 1/4" stainless steel tube with 1/32" diameter holes regularly spaced around the ring. The holes face in the downstream direction, which in the installed configuration is vertically upward. Prior to the selection of acetylene as the injected tracer gas, the potential for decomposition of acetylene at the potentially high temperatures in the dilution tunnel was investigated in well-stirred reactor simulations using Cantera software. Results suggested that the C_2H_2 should not react at the range of temperatures encountered experimentally. Subsequent experimental tests demonstrated that the injection of acetylene had no measureable effect on the combustion efficiency or species yields within the achievable measurement uncertainties when compared to data where no acetylene was injected.

2.5 Emissions Analysis Instrumentation

2.5.1 Gas-Phase Measurements and Gas-Phase Sample Train

Two instruments were used to measure gas concentrations in the current work. A MKS MultiGas 2030 Fourier Transform Infrared Spectrometer (FTIR) Continuous Gas Analyzer was the primary gas analysis instrument and a Los Gatos Research (LGR) Ultra-Portable Gas Analyzer was the secondary instrument for measuring concentrations of the tracer gas when it was present.

The FTIR instrument uses spectral absorption properties to measure up to 20 gas species simultaneously. The bias errors associated with measured concentrations of the gas species relevant to the current work are the larger of 2% of the measured value or the

minimum detection limit. The minimum detection limit for measured species are 0.15 ppm_v for CO, 0.10 ppm_v for CH₄, 0.15 ppm_v for C₂H₆, 0.30 ppm_v for C₃H₈ and C₂H₄, 0.50 ppm_v for NO and 0.05 ppm_v for NO₂. The lower detection limit for CO₂ was never encountered since measured concentrations were never below the threshold at which the 2% value was the controlling uncertainty. The LGR analyzer for measuring the acetylene tracer concentration has a bias error on the measured concentration of 2 ppb_v.

The sample train for the FTIR and the LGR analyzer are partially shared and will be discussed jointly as a gas-only sample train which is distinct from the soot sample train discussed in Section 2.5.2. The sample probe for this gas-only stream is a standard 1/4" diameter stainless steel tube. The open-ended tube is inserted vertically through the bottom surface of the duct to a depth of 353 mm (~86.9% of the total duct diameter) and has 1/8" holes drilled at 22, 71, 188 and 305 mm (~5.4, 17.5, 46.3 and 75.0% of total duct diameter) measured from the bottom surface of the duct (See Figure 2.3). The probe exits the duct vertically where the sample is split (using a tee-fitting) into two streams, one directed to the FTIR and the other to the LGR analyzer. The stream directed towards the FTIR connects from the tee-fitting to a 1/4" OD, 10-foot long Technical Heaters Inc. Series 500 flexible hose which is electrically heated to 191°C. The heated hose connects to a MKS-supplied, heated sample pump (also operated at 191°C) that contains a pair of filters to remove particulate so that the sample cell in the FTIR will not be contaminated. The pump exit connects to another 1/4" OD, 10-foot long Technical Heaters Inc. Series 702 flexible hose (also heated to 191°C) that connects to the measurement device. The LGR analyzer directed stream connects from the tee-fitting to 1/4" flexible nylon

tubing and is drawn by a dedicated internal pump installed in the analyzer. The stream directed to the LGR analyzer is also passed through a pair of filters for removal of particulate. An exposed length of the gas-probe extending approximately 5 cm from the bottom of the duct to the tee-fitting as well as the tee-fitting was also electrically heated to 191°C.

To satisfy the assumption of fully mixed conditions in the duct and ensure that the sampled concentrations were representative of the average concentrations, several traverses of a gas-sample probe were made across the duct diameter at different fan speeds and flare gas flow rates. As illustrated in Figure 2.4, gas-sample probe traverses were completed at a fan speed of 50% with flare gas flow rates of 27.36 and 136.81 SLPM and a fan speed of 100% with flare gas flow rates of 27.36 and 246.26 SLPM. At each probe position, the measured CO₂ concentration for five consecutive 1 minute FTIR scans are plotted. While there is some visible scatter in the measured concentrations at the higher flow rates, the average at a given probe position is well within the uncertainty on the average of all measurements for that fan speed and flare gas flow rate combination. These results demonstrate that the species in the exhaust system are well-mixed.

Figure 2.4: FTIR probe traverse CO₂ concentration measurements at 50% and 100% fan settings with low and high flare gas flow rates.

2.5.2 Soot Measurement with LII and Solid-Phase Sampling Train

An Artium 200 commercial Laser Induced Incandescence (LII) instrument was used to perform soot measurement in the current work. The LII device measures the soot volume fraction (SVF) present in a sampled volume. Only black carbon is measured as volatile particulate is sublimated by the laser energy.

The sample train connecting and controlling the flow of sample to the LII is partially depicted in Figure 2.5. The soot sampling probe installed in the duct as depicted in Figure 2.3 exits the bottom of the duct vertically and connects to a 5/16" ID, 10 foot Technical Heaters Inc. Series 212 fluoropolymer-lined flexible hose which is electrically heated to 65°C to limit thermophoretic losses of particulate to the wall. The probe itself is constructed of standard 3/8" diameter stainless steel tubing and with the tip bent 90° from the vertical. The bent portion was directed upstream during the tests and extends

125 mm in length from the centre of the vertical portion. The length of probe extending from the duct and connecting to the heated hose was also electrically heated to 65°C. The downstream end of the heated hose connected directly to the intake sample port of the LII. From the outlet sample port of the LII, the sample gas passed through an insulated tee fitting containing an exposed T-type thermocouple probe (Omega TC-T-NPT-E-72) that measured the temperature of the sample gas and allowed for the measured soot volume fraction to be corrected to the measured duct sample temperature as outlined by Eq. (3.18) in Section 3.3.4. Additional equipment on the downstream side of the LII sample train includes a filter for removing the soot and protecting downstream instruments, a Brooks 5851S digitally controlled MFC which maintained a controlled flow of sample through the LII, and a vacuum pump to draw a sample flow from the duct.

Figure 2.5: Rear of LII. Pictured components of sample train include a) heated hose, b) sample cell, c) outlet thermocouple, d) particulate filter, and e) MFC.

To satisfy the assumption of fully mixed conditions in the duct and to ensure the sampled SVF was consistent throughout the duct, several traverses across the duct diameter were made with the LII-sample probe at different fan speeds and flare gas flow rates. As illustrated in Figure 2.6, the LII-sample probe traverses were completed at a fan speed of 50% with a flare gas flow rate of 27.36 SLPM and a fan speed of 100% with flare gas flow rates of 27.36 and 267.54 SLPM. Measurements were conducted with the LII-sample probe facing both upstream and downstream to determine whether isokinetic sampling was necessary. Five consecutive 1 minute SVF measurements were made at each probe position and the results are plotted with the standard deviation of the 1 minute interval represented with the error bars. It is apparent that the SVF measured at each

location was consistent within expected error and that the orientation of the probe did not affect the measured SVF. These results demonstrate that the soot particles are well-mixed within the sample duct such that representative measurements can be obtained with single point samples.

Figure 2.6: LII probe traverse measurements at 50% and 100% fan settings with low and high flare gas flow rates.

2.6 Flame Imaging

Flame length was determined through analysis of static images (2048 x 1088 pixels) taken with a Basler acA2000-340km CMOS camera and acquired through a NI PCIe-1433 acquisition card. The camera was mounted to a sliding carriage on a vertical rail that allowed the camera to be repositioned appropriately for a given test condition. After installation, a checkered calibration sheet made up of alternating black and white 1" squares was suspended vertically in the plane of the burner. Images of the calibration sheet were taken from each of the preselected camera positions and an image correction

was applied using the common commercial software DaVis (LaVision GmbH) to account for image distortion away from the centreline of the image. Markers placed intermittently in the checker pattern of the calibration sheet allowed the height of a given pixel above the burner exit to be determined during the correction processing. Individual images of a test flame were binarized over a range of thresholds prior to the averaging of a set of images for each binarization threshold. Approximately 1500 images were used to determine flame length which was a large enough sample that the flame length for a given test converged to a consistent mean value. With the mean flame image, the length of a flame was arbitrarily defined as the measured distance between the burner exit and the highest pixel in which the flame was present for 10% of the images collected.

2.7 Sampling Protocol

A standard for performing measurements on the lab-scale flare was developed based on a review of previous sampling protocols and experience gained during the commissioning of the facility. The most important aspects of the sampling protocol were to measure ambient concentrations of relevant species before and after the test to ensure effective plume capture, to allow adequate warm-up time such that conditions reached a steady-state, and to monitor flare gas temperatures at the outlet of the thermal heating bath to ensure a consistent flow of the individual flare gas components. An additional consideration for experiments was a large outside door in the laboratory space in which the lab-scale flare was constructed. It was important that the door remained in either an open or closed state for the time leading up to and during a single test. This was deemed important as somewhat significant (50 – 100 ppm) changes in ambient CO₂ concentrations could occur if the door changed state (open to closed, closed to open)

during a test which impacted combustion efficiency and also plume flow rate calculations.

Measurement of relevant ambient concentrations (CO_2 , CO , NO , NO_2 , CH_4 , C_2H_6 , C_3H_8 , C_2H_4) in the laboratory were accomplished using the MKS FTIR gas-analyzer and taken for a period of at least 10 minutes both before and after each test. Ambient concentrations measured before each test were used in the calculations of combustion efficiency and species yields. Measurements of ambient concentrations taken after each test, primarily CO_2 , were used to verify that plume capture had been effective. This was determined based on the CO_2 concentration returning to the pre-test ambient value shortly after the flame was extinguished and flare gas flow stopped. It was observed that often hydrocarbon concentrations were high after the tests which are attributed to residual flare gas from the delivery line slowly purging.

The warm-up period to steady state criteria was evaluated based on a number of measured temperatures and concentrations. The criteria included measured temperatures for the duct sample probe, burner exit, LII sample, the methane flare gas at the exit of the thermal heating bath, and a position on the outside of the duct wall. The steady-state criteria for the various temperature measurements were a rate of increase less than 0.5°C per minute. The measured duct concentration of CO_2 was also considered and was deemed to have reached steady-state when the rate of change was less than 2% over the previous two FTIR scans. The 2% value corresponds to the expected uncertainty on a CO_2 measurement at the concentrations encountered. In cases where the LGR gas-analyzer was used in conjunction with an injected tracer gas, the tracer gas concentration reaching a steady-state value was an additional consideration. Both concentration

measurements implied a steady-state molar flow rate in the duct, and along with steady temperatures, implied a steady-state mass flow rate in the duct.

2.8 Methodology

The methodologies for evaluating the measurements in the current work are outlined in Chapter 3. The methods for evaluating combustion efficiency considering gas-phase species only and with the inclusion of a soot measurement are outlined in Sections 3.3.2 and 3.3.4 respectively. Similarly, all species yields calculated in the current work, which are calculated with the inclusion of a soot measurement in all instances, are outlined in Section 3.3.4.

Chapter 3

Detailed Expressions and Methodologies for Measuring Flare Combustion Efficiency, Species Emission Rates, and Associated Uncertainties

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This paper was co-authored by the thesis author, Darcy Corbin, and his M.A.Sc. supervisor Prof. Matthew Johnson. Mr. Corbin performed the initial derivations of all expressions, produced the synthetic data, and calculated the associated uncertainties. He also led construction on the Carleton Lab-Scale Flare facility and performed experimental measurements to produce the data considered in the analysis. Development of the concept of complementary methods for evaluating the performance of the combustion process, as well as writing and editing of the manuscript were performed jointly.

3.1 Abstract

Two complementary analytical methods for quantifying carbon conversion efficiency and species emission rates of gas flares in the form of turbulent non-premixed flames are derived and tested experimentally. Full mathematical expressions for partial derivative terms necessary to facilitate quantitative uncertainty analysis are also derived and presented as supplementary material. Key assumptions are individually tested and the

resulting generalized expressions are quantitatively compared with several other simplified expressions for calculating flare efficiency found in the literature. The first approach uses a carbon-balance approach to link measured concentrations of diluted combustion products to known flare gas outlet conditions while considering both the dilution of the combustion products and ambient levels of relevant species in the dilution and combustion air. This method is further extended to allow explicit consideration of solid-phase black carbon (soot) that may be present in the products. A second distinct method utilizes a tracer gas injected into the diluted plume to enable quantification of species emission rates from the combustion process directly. Experiments reveal how the two approaches each have advantages in different situations allowing experiments to be better optimized to reduced uncertainties. In addition, the tracer injection method is extensible for use in quantifying efficiencies and liquid-fallout on flares burning a mixed-phase fuel stream.

3.2 Introduction

Flaring is the practice of burning unusable or unwanted flammable gas which might otherwise be vented directly to the atmosphere. Ideally, the combustion process would convert 100% of fuel-bound carbon to carbon dioxide. However, under certain conditions (e.g. strong crosswind, low heating value, excess steam- or air-assist) the carbon conversion efficiency can be reduced (Johnson, Wilson, et al., 2001; Johnson and Kostiuk, 2000; Johnson and Kostiuk, 2002; Torres, Herndon, Kodesh, et al., 2012; Torres, Herndon, and Allen, 2012; Pohl et al., 1986) and the portion of unburned or partially reacted species leaving the flare can increase. Of particular interest are the potential release of unburned methane (Johnson, Wilson, et al., 2001) and black carbon

(McEwen and Johnson, 2012; Johnson et al., 2011; Johnson et al., 2013), both of which are potent short-lived climate forcing agents (IPCC, 2013).

This paper develops and critiques analytical methods for calculating carbon conversion efficiencies and species emission rates from unconfined, non-premixed jet flames using gas and particulate samples collected from the plume. The methods each use a system of species conservation equations considering various plume constituents to determine the overall rate of conversion of fuel-bound carbon to carbon dioxide. The robustness of the methods was analyzed using prescribed synthetic test data to mimic the combustion process over a range of anticipated potential conditions, and subsequently tested in lab-scale experiments. A quantitative uncertainty analysis was also performed for the various test conditions and the appropriateness of each method for use in further lab and field experiments is discussed.

3.3 Theory

Combustion efficiency, η , can be defined in different ways, however, for the current analysis it will be defined as carbon conversion efficiency which compares the mass of fully oxidized carbon (i.e. mass of carbon within carbon dioxide) produced by combustion to the mass of carbon in the form of hydrocarbons in the fuel stream (Bourguignon et al., 1999):

$$\eta [\%] = \frac{\text{mass of carbon in produced } CO_2}{\text{mass of carbon in hydrocarbon fuel stream}} \times 100 \quad (3.1)$$

It is noted that for cases where $\eta < 100\%$, this definition does not impose any restrictions on the composition or phase of incomplete combustion products. In general

these products may include gas phase species such as carbon monoxide and unburned or reformed hydrocarbons, as well as particulate phase soot. In some situations, it may also be useful to define a destruction removal efficiency of any combustible species i in the fuel stream (DRE_i) as:

$$DRE_i [\%] = \left(1 - \frac{\text{production rate of species } i}{\text{flow rate of species } i \text{ in the fuel stream}} \right) \times 100 \quad (3.2)$$

3.3.1 General Combustion Efficiency and Species Conservation Equations

Incomplete combustion of a general hydrocarbon fuel or fuel blend (C_xH_y) can be summarized with the following global combustion equation:

The potential products of incomplete combustion may take the form of carbon monoxide (CO), unburned methane (CH_4), unburned and/or reformed gas-phase non- CH_4 hydrocarbons (C_mH_n), and carbon in the form of soot ($C_{(s)}$). It is noted that the form of any unburned hydrocarbon species is not restricted to the same form as the hydrocarbons entering in the fuel stream (C_xH_y) or entrained in the ambient air. The summation term, $\sum_{m,n} g_{m,n}C_mH_n$, is thus used to represent all produced non- CH_4 hydrocarbons. The utility of separating CH_4 and $C_{(s)}$ from C_mH_n in Eq. (3.3) will become apparent further in the development where $C_{(s)}$ may be neglected for the purpose of considering gas-phase-only species, and where the influence of ambient concentrations of CH_4 may be directly considered while ambient concentrations of other species are deemed negligible.

Figure 3.1 shows a schematic of an arbitrary control volume (CV, represented by the dashed blue line) enclosing the flame, within which all chemical reactions and product dilution occur. The figure introduces various mass flow rates ($\dot{m}$) that are important to consider for use throughout the manuscript. Flare gas ($\dot{m}_{FG}$), and an unknown flow rate of ambient air ($\dot{m}_{\infty}$), enter the CV. Inside the CV, the flare gas is split into hydrocarbons ($\dot{m}_{C_xH_y,FG}$) and diluents ($\{\dot{m}_{FG}\}_{inert}$) that may be present. The ambient air is split into air involved directly in the combustion process ($\dot{m}_{combustion\ air}$) and air entrained during subsequent dilution of the combustion products ($\dot{m}_{dilution\ air}$). The two constituents of the flare gas stream combine with the combustion air and react to release a variety of combustion products ($\dot{m}_{produced}$) as well as any inert species originating in the flare gas. The products are then diluted by the remainder of the ambient air entering the control volume before exiting as the overall plume flow rate ($\dot{m}_{plume}$).

Figure 3.1: Control volume (CV, indicated by dashed blue line) for combustion process illustrating the overall mass balance defined by Eq. (3.4) (sum of terms outside CV) and the breakdown of terms relevant to the species mass balance defined by Eq. (3.5) . Red arrows indicate terms containing products of combustion.

By considering the CV shown in Figure 3.1, an expression for the overall mass balance can be derived as follows:

$$\dot{m}_{plume} = \dot{m}_{FG} + \dot{m}_{\infty} \quad (3.4)$$

Although the present equations are derived with the intent of evaluating combustion from non-premixed turbulent diffusion flames such as gas flares, the application of the CV illustrated in Figure 3.1 and the overall mass balance defined by Eq. (3.4) are not necessarily restricted to non-premixed combustion. Since the choice of CV does not specify whether the mixing of fuel and oxidizer occur across a flame front, as in a non-premixed configuration, or upstream of the flame, as in a premixed flame, the developed equations may thus be extended to any general hydrocarbon / oxygen combustion system.

Similarly, a species mass balance can be developed for individual species relevant to the combustion process. The mass emission rate of a species i as a component of the diluted combustion products can be written as $Y_{i,plume}\dot{m}_{plume}$, where Y is mass fraction and $Y_{i,plume}$ represents the mass fraction of species i in the diluted plume. The specific species emission rate will depend on the chemical production rate (positive or negative) of species i , $\dot{m}_{i,produced}$; the potential emissions of species i as an inert component of the fuel (i.e. as would occur in a fuel stream containing CO₂ diluent), $\{Y_{i,FG}\dot{m}_{FG}\}_{inert}$; and the rate at which species i is entrained into the plume as an ambient constituent of the entrained air, $Y_{i,\infty}\dot{m}_{\infty}$.

$$Y_{i,plume}\dot{m}_{plume} = \dot{m}_{i,produced} + \{Y_{i,FG}\dot{m}_{FG}\}_{inert} + Y_{i,\infty}\dot{m}_{\infty} \quad (3.5)$$

Eq. (3.5) implicitly assumes that any trace species (e.g. hydrocarbons or CO_2) present in the combustion air as a constituent of $\dot{m}_\infty$ do not react. Any potential contribution to the species mass balance due to reactions of these trace species in the combustion air would be negligible relative to the mass of these same species present in air entrained into the plume (Poudenx, 2000). Eq. (3.5) further assumes that the constituents of the plume are well mixed such that the composition may be described using a single mass fraction for each species. This well-mixed state is readily achieved in the present experiments where the entire plume is captured and mixed in a duct prior to sampling, and the implications for other sampling systems are further discussed in Section 3.3.2 below.

3.3.2 Combustion Efficiency and Species Emission Rates Assuming Gas Phase Only Combustion Products

The initial base case for analysis considers gas-phase products of combustion only, and inherently assumes that any non-gaseous species have negligible contribution to the overall carbon mass balance. This scenario is relevant to flares burning primarily ‘light’ methane-based solution gas, which is a typical flare gas composition in the upstream oil and gas industry (Johnson and Coderre, 2012). Available experimental data for turbulent non-premixed flames burning light hydrocarbon fuels confirm that the proportion of carbon mass emitted in the form of soot is likely negligible. Furthermore, experiments by Pohl et al. (1986) on propane- and propane/nitrogen-fueled vertical diffusion flames established on 3-12” diameter flare burners suggest that soot accounts for less than 0.5% of the fuel carbon mass for these flames. More recent experiments (McEwen and Johnson, 2012) on lab-scale flares (1-2” diameter) burning primarily methane mixtures consistent with compositions entering solution gas flares in the Alberta upstream

petroleum industry (Johnson and Coderre, 2012), suggest that soot will account for no more than 0.1% of the combusted carbon by mass.

By considering only gas phase products of combustion, Eq. (3.3) simplifies to:

Using the relationship between mole and mass fractions, Eq. (3.5) can be more conveniently written in molar form since typical gas analyzers measure volume or mole fraction:

$$X_{i,plume}\dot{n}_{plume} = \dot{n}_{i,produced} + \{X_{i,FG}\dot{n}_{FG}\}_{inert} + X_{i,\infty}\dot{n}_{\infty} \quad (3.7)$$

where X_i denotes the mole fraction of species i , and $\dot{n}$ denotes molar flow rate. The definition of combustion efficiency, Eq. (3.1), can similarly be rewritten in molar form where $X_{C_xH_y,FG}$ is the mole fraction of hydrocarbon C_xH_y in the fuel stream and x is the relevant carbon coefficient:

$$\eta [\%] = \frac{\dot{n}_{CO_2,produced}}{x \left(X_{C_xH_y,FG} \right) \dot{n}_{FG}} \times 100 \quad (3.8)$$

Destruction efficiency can also be expressed in molar form where $X_{i,FG}$ is the mole fraction of species i in the fuel stream:

$$DRE [\%] = \left(1 - \frac{\dot{n}_{i,produced}}{X_{i,FG}\dot{n}_{FG}} \right) \times 100 \quad (3.9)$$

In the current lab-scale experiment, the flare is centred under a large collection hood connected to a variable speed exhaust extraction system. The flow rate of the exhaust plume can be directly controlled to provide the lowest possible dilution for a given fuel flow rate, while still capturing the entire product plume. The sampling point is more than 10 metres downstream of the duct entrance and, during commissioning of the facility, sample probes were traversed across the duct to verify that gas species mole fractions and soot volume fractions were consistent across the diameter over the range of test conditions.

More generally, in other laboratory setups or especially in field measurement scenarios, it is likely impossible to capture the entire plume. If only a portion of the plume is captured for sampling (e.g. as would occur if single point samples were drawn from a region of the plume), then Eq. (3.5) can still be applied so long as the measured species mole fractions in the captured portion of the plume are assumed to be equal to the mean species mole fractions of the entire plume. Alternatively, the developed equations remain valid for determining local combustion or destruction removal efficiencies at a point in the plume, although it should be noted that the relationship between local and overall efficiencies is not necessarily straightforward if spatial variations in velocity and species concentrations in the plume are significant. While experiments in low-turbulence wind tunnels (Poudenx, 2000) have shown that the plume of a lab-scale flare may be quite inhomogeneous in the near field of the flame (sampling from 1.17 to 1.38 flame lengths downstream of burner exit), these same data suggest that samples drawn from a central region of the plume are representative of the plume as a whole. This latter approach was used in recent field measurements (Allen and Torres, 2011) where a

50.8 cm sample intake was used to capture 15-20% of the product volume at several metres (>2 flame lengths) from the burner exit. The sampling system was designed with the intent of sampling a large volume of plume and forcing mixing before the sample was measured. Although possible inhomogeneity of the plume as a function of sampling location was not investigated (Herndon et al., 2012), additional review of the results from this study suggest that the relative levels of carbon-based species (ratio of CO to CO₂ for example) in the measured plume were well-correlated and independent of time and dilution.

The gas-phase species mole fractions of relevant species in the diluted plume: X_{CO_2} , X_{CO} , X_{CH_4} , $X_{C_mH_n}$ are all directly measureable using gas analyzers. The flow rate and composition of flare gas are also directly measureable, meaning x , $X_{C_xH_y,FG}$, $\{X_{i,FG}\}_{inert}$, M_{FG} , and $\dot{n}_{FG}$ are also known. By rearranging Eq. (3.7) in terms of the species production rate and combining with Eq. (3.4) to eliminate the entrained air term, a carbon balance can be derived in which the only unknown term is the plume flow rate.

$$x(X_{C_xH_y,FG})\dot{n}_{FG} = \sum_i \#_{C,i} \left(X_{i,plume} - X_{i,\infty} \frac{M_{plume}}{M_\infty} \right) \dot{n}_{plume} + \sum_i \#_{C,i} \left(X_{i,\infty} \frac{M_{FG}}{M_\infty} \dot{n}_{FG} \right) - \{X_{CO_2,FG}\dot{n}_{FG}\}_{inert} \quad (3.10)$$

where $\#_{C,i}$ indicates the number of carbons per molecule of each species in the plume (ie. $\#_{C,i} = 1$ for CO₂ and $\#_{C,i} = m$ for C_mH_n) and CO₂ is assumed to be the only potential carbon-based inert species in the flare gas.

Eq. (3.10) explicitly considers species mole fractions measured in the plume, the exact dilution of the products of combustion, and the contribution by ambient species in the entrained air to the determination of combustion efficiency.

However the overall mass balance brings in the molecular mass of the plume, M_{plume} , which is unknown and depends on the dilution ratio (where dilution ratio is defined as the volume of air diluting the combustion products over the volume of combustion products) and specific chemical composition of the products. If gas analyzers are capable of measuring water vapour in the plume, M_{plume} can be directly calculated based on the measured volume fraction of CO_2 , CO , CH_4 , C_mH_n , and H_2O with the assumption that the ratio of N_2 to O_2 in the atmosphere is fixed. Alternatively, it is simpler and ultimately accurate to assume that the molecular mass of the plume is equivalent to that of the ambient air. Even at a low dilution ratio of 10 (which would be difficult to achieve in a practical experiment), the deviation in calculated molar mass of the plume versus that of air is less than 0.5% for flare efficiencies above 80%. The influence of this assumption is further damped in the calculation of efficiency, such that the resultant absolute bias error in the calculated efficiency is less than 5×10^{-3} at an efficiency of 80% and dilution ratio of 10. The effect of assuming $M_{plume} = M_\infty$ is even less pronounced at higher efficiencies and/or higher dilution ratios. With the assumptions that $M_{plume} = M_\infty$ the plume flow rate can be explicitly solved for as shown below.

$$\dot{n}_{plume,gas} = \frac{x \left(X_{C_xH_y,FG} \right) \dot{n}_{FG} + X_{CO_2,FG} \dot{n}_{FG} - \left(X_{CO_2,\infty} + X_{CO,\infty} + X_{CH_4,\infty} + \sum_{m,n} \#_{C,C_mH_n} X_{C_mH_n,\infty} \right) \frac{M_{FG}}{M_\infty} \dot{n}_{FG}}{X_{CO_2,plume} - X_{CO_2,\infty} + A} \quad (3.11)$$

$$\text{where } A = \left(X_{CO,plume} - X_{CO,\infty} + X_{CH_4,plume} - X_{CH_4,\infty} + \sum_{m,n} \#_{C,C_mH_n} (X_{C_mH_n,plume} - X_{C_mH_n,\infty}) \right)$$

By substituting the plume flow rate into the species balance equation for CO₂, the efficiency defined in Eq. (3.8) can be expressed explicitly as:

$$\eta [\%] = \frac{x(X_{C_xH_y,FG})B - X_{CO_2,FG}A + (X_{CO_2,\infty}D - X_{CO_2,plume}(X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,C_mH_n} X_{C_mH_n,\infty})) \frac{M_{FG}}{M_{\infty}}}{x(X_{C_xH_y,FG})(X_{CO_2,plume} - X_{CO_2,\infty} + A)} \times 100 \quad (3.12)$$

where $A = (X_{CO,plume} - X_{CO,\infty} + X_{CH_4,plume} - X_{CH_4,\infty} + \sum_{m,n} \#_{C,C_mH_n} (X_{C_mH_n,plume} - X_{C_mH_n,\infty}))$,
 $B = (X_{CO_2,plume} - X_{CO_2,\infty})$, and
 $D = (X_{CO,plume} + X_{CH_4,plume} + \sum_i \#_{C,C_mH_n} X_{C_mH_n,plume})$.

In Eq. (3.12), it can be noted that all rate terms (fuel hydrocarbon flow rate and gross fuel flow rate) have been removed from the equation and only rate independent mole fractions remain. The conversion efficiency is thus a function of the carbon-based species mole fractions in the plume and ambient air as well as the flare gas composition.

With the plume flow rate defined per Eq. (3.11), the emission rate of any species, whether carbon-based or not (e.g. nitric oxide), can be determined by rearranging Eq. (3.7) as follows.

$$\dot{m}_{i,produced} = M_i \left((X_{i,plume} - X_{i,\infty}) \dot{n}_{plume,gas} - \left\{ X_{i,FG} \frac{\dot{m}_{FG}}{M_{FG}} \right\}_{inert} + X_{i,\infty} \frac{\dot{m}_{FG}}{M_{\infty}} \right) \quad (3.13)$$

Using Eq. (3.13) and the plume flow rate defined by Eq. (3.11), the destruction removal efficiency (DRE_i) of any combustible species i present in the flare gas can be defined as:

$$DRE_i [\%] = \left(1 - \frac{\left(x(X_{C_xH_y,FG}) + X_{CO_2,FG} \right) (X_{i,plume} - X_{i,\infty}) + (X_{i,\infty} (X_{CO_2,plume} + D) - X_{i,plume} (X_{CO_2,\infty} + E)) \frac{M_{FG}}{M_{\infty}}}{(X_{i,FG})(X_{CO_2,plume} - X_{CO_2,\infty} + A)} \right) \times 100 \quad (3.14)$$

where $A = (X_{CO,plume} - X_{CO,\infty} + X_{CH_4,plume} - X_{CH_4,\infty} + \sum_{m,n} \#_{C,C_mH_n} (X_{C_mH_n,plume} - X_{C_mH_n,\infty}))$,

$D = (X_{CO,plume} + X_{CH_4,plume} + \sum_i \#_{C,C_mH_n} X_{C_mH_n,plume})$, and

$E = (X_{CO,\infty} + X_{CH_4,\infty} + \sum_{m,n} \#_{C,C_mH_n} X_{C_mH_n,\infty})$.

In cases where the combustion efficiency is suitably high, it may be sufficiently accurate and simpler to assume 100% combustion efficiency when calculating the plume flow rate. In this case the carbon balance for combustion considers only CO₂ as a product, and Eq. (3.11) simplifies to:

$$\dot{n}_{plume,100\%} = \frac{x(X_{C_xH_y,FG}) \dot{n}_{FG} + X_{CO_2,FG} \dot{n}_{FG} - X_{CO_2,\infty} \frac{M_{FG}}{M_{\infty}} \dot{n}_{FG}}{(X_{CO_2,plume} - X_{CO_2,\infty})} \quad (3.15)$$

The assumption of 100% combustion efficiency can then be relaxed, and Eq. (3.15) used instead of Eq. (3.11) in combination with Eq. (3.13) to derive production rates of other species from their change in measured mole fractions in the plume relative to ambient.

Quantification of the uncertainty in the measured plume flow rate defined by Eq. (3.11), combustion efficiency defined by Eq. (3.12), gaseous species mass emission rate defined by Eq. (3.13), and flare gas species destruction removal efficiency Eq. (3.14) can be accomplished using expressions developed in the supplementary material. The uncertainty on combustion efficiency can be calculated following the instructions in Section A1 with systematic error defined by Eq. (A.5). For plume flow rate, the uncertainty can be evaluated following the instructions in Section A2 with

systematic error defined by Eq. (A.7). The uncertainty of gas-phase species emission rates can be calculated following the instructions in Section A4.1 for non-carbon-based species, or Section A4.2 for carbon-based species with systematic error defined by Eq. (A.10) or Eq. (A.13) respectively. Similarly, the systematic error for the DRE of a non-carbon-based flare gas species is defined by Eq. (A.12) and of a carbon-based flare gas species by Eq. (A.15).

3.3.3 Comparison with Simplified Expressions for Combustion Efficiency used in Other Works

A number of different expressions for efficiency have been employed by previous researchers, each of which relies on various simplifications to the method outlined above. The simplifications range from neglecting only the ambient species present in the combustion air to neglecting all ambient concentrations completely, and none of these methods is directly applicable to fuel streams which contain CO₂. To the authors' knowledge, no previous studies have attempted a comprehensive uncertainty analysis of the methods employed, with the possible exception of Bourguignon et al. (1999) who considered the uniquely specific problem of flare efficiency measurements in a closed-loop windtunnel. This is not necessarily surprising given the inherent difficulty in fully accounting for entrained ambient species in situations where sampling rates, entrainment rates, and combustion efficiency are all unknown. One of the most robust analysis of combustion efficiency found in the literature (Poudenx, 2000) neglects the presence of ambient species in the combustion air itself and the possibility of CO₂ as a fuel diluent. An oxygen balance is used to estimate a product dilution factor and corrects the contribution of ambient species to plume levels using this factor. Similarly, the method employed by Pohl et al. (1986) corrects for the influence of ambient species

concentrations on measured plume dilution by using the theoretical production/consumption of carbon dioxide or oxygen assuming complete combustion to determine a dilution factor. In the mid-1980s EPA flare study (McDaniel, 1983), ambient concentrations of all major species were considered by directly subtracting background levels from measured plume values, although the mass balance includes a minor assumption that the volume of combustion air and the ambient species entrained with it are negligible compared to amounts entrained for dilution. In the efficiency calculations shown in the published overview of the recent TCEQ flare study (Allen and Torres, 2011), only ambient CO₂ was considered (Torres, Herndon, Kodesh, et al., 2012) while other ambient species were neglected. The equation for combustion efficiency for lab-scale and field measurements reported by Strosher (2000) includes no explicit correction for ambient concentrations of carbon-containing species. The combustion efficiency expressions used in the respective studies are summarized in Table 3.1.

Table 3.1: Various combustion efficiency expressions

McDaniel (1983)	$\frac{X_{CO_2,plume} - X_{CO_2,\infty}}{X_{CO_2,plume} - X_{CO_2,\infty} + X_{CO,plume} - X_{CO,\infty} + \sum_{m,n} \#_{C,C_mH_n} X_{C_mH_n,plume} - \sum_{m,n} \#_{C,C_mH_n} X_{C_mH_n,\infty} + Soot}$
Pohl et al. (1986)	$\frac{(DF + 1)X_{CO_2,plume} - (DF)X_{CO_2,\infty}}{(DF + 1)(X_{CO_2,plume} + X_{CO,plume} + \sum_{m,n} \#_{C,C_mH_n} X_{C_mH_n,plume} + Soot) - (DF)(X_{CO_2,\infty} + X_{CO,\infty} + \sum_{m,n} \#_{C,C_mH_n} X_{C_mH_n,\infty})}$ <p style="text-align: center;">where $DF = \frac{X_{I,plume} - X_{I,SR=1,theoretical}}{X_{I,\infty} - X_{I,plume}}$</p>
Poudenx (2000)	$\frac{X_{CO_2,plume} - (1 - \alpha)X_{CO_2,\infty}}{X_{CO_2,plume} + X_{CO,plume} + \sum_{m,n} \#_{C,C_mH_n} X_{C_mH_n,plume} - (1 - \alpha)(X_{CO_2,\infty} + X_{CO,\infty} + \sum_{m,n} \#_{C,C_mH_n} X_{C_mH_n,\infty})}$ <p style="text-align: center;">where $\alpha = 1 - \frac{X_{O_2,plume}}{X_{O_2,\infty}}$</p>
Strosher (2000)	$\frac{X_{CO_2,plume}}{X_{CO_2,plume} + X_{CO,plume} + \sum_{m,n} \#_{C,C_mH_n} X_{C_mH_n,plume} + Soot}$
Torres, Herndon, Kodesh, et al. (2012)	$\frac{X_{CO_2,plume} - X_{CO_2,\infty}}{X_{CO_2,plume} - X_{CO_2,\infty} + X_{CO,plume} + \sum_{m,n} \#_{C,C_mH_n} X_{C_mH_n,plume}}$

The effect of neglecting or partially neglecting ambient concentrations on the calculated efficiency will vary with both the level of ambient species and the dilution of the products with entrained air. Each species in the efficiency equations of Table 3.1 is implicitly or explicitly multiplied by its respective carbon number, $\#_{C,i}$. CO_2 , CO , and CH_4 each has a carbon number of one (one carbon atom per molecule), while $\#_{C,i} > 1$ for higher hydrocarbons. Thus, the effect of neglecting one ambient CO molecule is equivalent to neglecting one CH_4 molecule, with each having half the effect of an ethane (C_2H_6) molecule ($\#_{C,i} = 2$). Figure 3.2a shows the discrepancy between efficiencies calculated using the equations above and the actual efficiency as a function of dilution ratio assuming nominal ambient concentrations of $\text{CO}_2 = 400\text{ppm}_v$, $\text{CO} = 1.5\text{ppm}_v$ (US EPA, 2013a), and $\text{CH}_4 = 1.8\text{ppm}_v$ (US EPA, 2013b). Figure 3.2b shows the different bias errors incurred if CO_2 is present in the flare gas at 5% by volume. The efficiency expressions defined by McDaniel (1983) and Pohl et al. (1986) have distinct bias errors, however the differences are negligible over the conditions shown in Figure 3.2. Although the maximum dilution ratio in the present experiments is 216, recent airborne field measurements using highly sensitive cavity ringdown gas analyzers (Caulton et al., 2014) suggests that dilution ratios of 1000 or more may be relevant in other settings.

Figure 3.2: Potential bias errors incurred when using different efficiency expressions (McDaniel (1983), Pohl et al. (1986), Torres, Herndon, Kodesh, et al. (2012), Stroscher (2000)) as a function of dilution ratio for nominal ambient concentrations of $\text{CO}_2=400\text{ppm}_v$, $\text{CO}=1.5\text{ppm}_v$, and $\text{CH}_4=1.8\text{ppm}_v$, where the flare gas contains (a) no CO_2 ; (b) 5% CO_2 .

For all of the methods, increased ambient levels of any species that are present as products of incomplete combustion and not corrected for in the equations will result in additional underestimation of the combustion efficiency. Similarly, increased levels of carbon dioxide in the ambient air will result in overestimation of combustion efficiency for methods that do not explicitly include correction for ambient CO_2 levels. If carbon dioxide were present as a fuel diluent this would induce further bias as it is unaccounted for in the final forms of the equations shown above. Across all dilution ratios and levels of carbon dioxide diluent, the generalized method derived in this paper is able to determine gaseous combustion efficiency within a maximum bias error of less than $5 \cdot 10^{-3}$ % (e.g. efficiency [%] of 95 ± 0.005).

3.3.4 Combustion Efficiency and Species Emission Rates with In Situ Black Carbon Measurement

The calculation approach derived in Section 3.3.2 can be further extended to include direct measurements of emitted carbon mass in the form of soot. Revised species

balances as well as a general mass balance are used to produce a carbon balance, which allows for closed forms of plume flow rate, combustion efficiency, and species production rates to be developed. This method includes the same assumptions as the gaseous-phase-only equations derived in Section 3.3.2, namely non-reacting ambient species, the molar mass of the plume being equivalent to the ambient value, along with the additional assumption that ambient levels of soot in the entrained air can be neglected. The global combustion expression given by Eq. (3.3) is utilized, which includes all gas species as well as soot, resulting in mixed-phase products. In the present analysis soot is considered as solid phase molecular carbon, which is consistent with measurements made with laser induced incandescence (LII).

The species balance equation for soot is:

$$\rho_{C(s)} f_{v,plume} \dot{Q}_{plume} = M_{C(s)} \dot{n}_{C(s),produced} \quad (3.16)$$

where $f_{v,plume}$, is the soot volume fraction in the plume which may be measured using LII or other techniques and $\rho_{C(s)}$ is the density of soot which has an assumed (Johnson et al., 2013) value of 1860 kg/m³ with an approximate normally distributed standard deviation of 120 kg/m³.

Using the carbon balance technique outlined in a previous section, the plume flow rate can be modified for the inclusion of produced soot:

$$\dot{n}_{plume,gas} = \frac{x(X_{C_xH_y,FG})\dot{n}_{FG} + X_{CO_2,FG}\dot{n}_{FG} - (X_{CO_2,\infty} + X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,C_mH_n} X_{C_mH_n,\infty}) \frac{M_{FG}}{M_\infty} \dot{n}_{FG}}{X_{CO_2,plume} - X_{CO_2,\infty} + \frac{\rho_{C(s)} f_{v,plume} R_u T_{plume}}{M_{C(s)} P_{plume}} + A} \quad (3.17)$$

$$\text{where } A = (X_{CO,plume} - X_{CO,\infty} + X_{CH_4,plume} - X_{CH_4,\infty} + \sum_{m,n} \#_{C,C_mH_n} (X_{C_mH_n,plume} - X_{C_mH_n,\infty})).$$

In Eq. (3.17) , it is implicitly assumed that the sampled volume of soot particles is negligible relative to the sampled gas volume, such that gaseous species mole fractions obtained using typical gas analyzers which require filtered samples free from particulate, are equal to the mole fractions in an unfiltered sample. This is quite reasonable given that measured volume fractions of soot in the plume are typically of the order of parts per million or less. It is further noted that the use of Eq. (3.17) requires measurement of the plume temperature, T_{plume} , and static pressure, P_{plume} , which are necessary to convert the measured soot volume fraction to moles of carbon. Additionally, a correction to the soot volume fraction measured by the LII (or other instrument) must be made to account for differences in temperature between the measurement cell and the plume (McEwen, 2010) as defined below.

$$f_{v,plume} = f_{v,measured} \frac{T_{measured}}{T_{plume}} \quad (3.18)$$

From Eq. (3.17) and Eq. (3.18) , the new closed form equation below can be developed to evaluate combustion efficiency with the inclusion of direct soot measurement.

$$\eta [\%] = \frac{x(X_{C_xH_y,FG})B - X_{CO_2,FG}F + (X_{CO_2,\infty}G - X_{CO_2,plume}(X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,C_mH_n} X_{C_mH_n,\infty})) \frac{M_{FG}}{M_{\infty}}}{x(X_{C_xH_y,FG})(X_{CO_2,plume} - X_{CO_2,\infty} + F)} \times 100 \quad (3.19)$$

where $B = (X_{CO_2,plume} - X_{CO_2,\infty}),$

$$F = (X_{CO,plume} - X_{CO,\infty} + X_{CH_4,plume} - X_{CH_4,\infty} + \sum_{m,n} \#_{C,C_mH_n} (X_{C_mH_n,plume} - X_{C_mH_n,\infty}) + H),$$

$$G = (X_{CO,plume} + X_{CH_4,plume} + \sum_i \#_{C,C_mH_n} X_{C_mH_n,plume} + H), \text{ and}$$

$$H = \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}}.$$

Similar to the scenario in which only gas-phase species are considered, using Eq. (3.13) and the plume flow rate defined by Eq. (3.17), the destruction removal efficiency (DRE_i) of any combustible species i present in the flare gas can be defined as:

$$DRE_i [\%] = \left(1 - \frac{\left(x \left(X_{C_xH_y,FG} \right) + X_{CO_2,FG} \right) \left(X_{i,plume} - X_{i,\infty} \right) + \left(X_{i,\infty} \left(X_{CO_2,plume} + G \right) - X_{i,plume} \left(X_{CO_2,\infty} + E \right) \right) \frac{M_{EG}}{M_{\infty}}}{X_{i,FG} \left(X_{CO_2,plume} - X_{CO_2,\infty} + F \right)} \right) \times 100 \quad (3.20)$$

where $E = (X_{CO,\infty} + X_{CH_4,\infty} + \sum_{m,n} \#_{C,C_mH_n} X_{C_mH_n,\infty})$,

$$F = (X_{CO,plume} - X_{CO,\infty} + X_{CH_4,plume} - X_{CH_4,\infty} + \sum_{m,n} \#_{C,C_mH_n} (X_{C_mH_n,plume} - X_{C_mH_n,\infty}) + H),$$

$$G = (X_{CO,plume} + X_{CH_4,plume} + \sum_i \#_{C,C_mH_n} X_{C_mH_n,plume} + H), \text{ and}$$

$$H = \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}}.$$

Production rates for a general gas species can be calculated using Eq. (3.13) using the plume flow rate term defined by Eq. (3.17). Finally, the production rate of soot can be directly calculated as:

$$\dot{m}_{C(s),produced} = \rho_{C(s)} f_{v,measured} \frac{R_u T_{sample}}{P_{plume}} \dot{n}_{plume,gas} \quad (3.21)$$

Quantification of the uncertainty in the measured plume flow rate defined by Eq. (3.17), combustion efficiency defined by Eq. (3.19), DRE defined by Eq. (3.20), and black-carbon emission rate defined by Eq. (3.21) can be accomplished using expressions developed in the supplementary material. The uncertainty on combustion efficiency can be calculated following the instructions in Section S.1 with systematic error defined by Eq. (A.5). The uncertainty on the plume flow rate can be calculated following the instructions in Section A2 with systematic error defined by Eq. (A.7). For

black carbon emission rate, the uncertainty can be evaluated following the instructions in Section A4.2 with the systematic error defined by Eq. (A.14).

3.3.5 Efficiency Measurements Using a Tracer Injection for Plume Flow Rate Measurement

Although the generalized carbon balance methods outlined in Sections 3.3.2 and 3.3.3 are suitable for a wide variety of applications, there are cases where an alternate method is desirable, which does not rely on an explicit carbon balance as in Eq. (3.10). This would include a situation in which the fuel stream contains a significant liquid fraction that may pass through the flame without burning, and subsequently fall to the ground rather than being entrained with the product plume. Closing the carbon balance via direct measurement of all emitted carbon containing species would not be practically feasible in this situation. However, a substitute equation to use with the system of mass balance equations can be derived following an injection of a non-reacting, measurable gas tracer species into the sampling system that is otherwise not present at appreciable concentrations in ambient air or the products of combustion. Depending on the available measurement technology, it may also be possible to achieve lower overall uncertainties via a tracer-based approach as demonstrated in Section 3.5.

By injecting the gaseous tracer directly into the sampling duct, a simple species mass balance for determining the gas flow rate of the sampled plume can be derived, Eq. (3.22), and used to directly quantify the molar flux of captured plume (and hence the molar flux of captured fuel-based carbon).

$$\dot{n}_{plume,gas} = \frac{\frac{\dot{m}_{tracer}}{M_{tracer}} (1 - X_{tracer}^*)}{(X_{tracer} - X_{tracer}^*)} \quad (3.22)$$

In Eq. (3.22) , X_{tracer} is the measured mole fraction of tracer in the sampling duct while the tracer is being injected, and X_{tracer}^* is the mole fraction of tracer in the plume prior to tracer injection (i.e. when $\dot{m}_{tracer} = 0$). Depending on the choice of tracer species, this background term may be negligible. The uncertainty in the measured plume flow rate, defined by Eq. (3.22) , can be quantified following the instructions in Section S.3 of the supplemental material with systematic error defined by Eq. (A.8). Corresponding uncertainties in gas-phase species or black-carbon emission rates (defined by Eq. (3.13) and Eq. (3.21)), where the plume flow rate is calculated using the tracer-injection method, can be quantified following the instructions in Section A4.1 with systematic error defined by Eq. (A.10) or Eq. (A.11) for gas-phase species and black carbon respectively. The uncertainties in flare gas species DRE can be quantified following the instructions in Section A4.1 with systematic error defined by Eq. (A.12).

In an experiment where 100% of the plume-borne carbon is captured (gas and particulate phase), the plume molar flow rate defined in Eq. (3.22) can be used in conjunction with Eq. (3.13) to calculate species emission rates, which can then be used to determine combustion efficiency via Eq. (3.8) . Similarly, the destruction removal efficiency for a given flare gas species (Eq. (3.2)) may be calculated using Eq. (3.13) in conjunction with Eq. (3.22) to calculate the production rate, and dividing by the flow rate of that species in the flare gas. As shown in the results, this method may lead to reduced uncertainties in calculated species production rates depending on the dilution ratio of the sample and the relative concentrations of species in the plume being measured. Furthermore, as noted above, this tracer-based measurement technique could be utilized with a sampling system capable of capturing 100% of the plume-borne carbon (i.e.

gaseous species and soot) to quantify hydrocarbon fallout if liquid constituents were present in the flare stream. In this scenario, the fuel to product mass balance could be closed by directly measuring the plume flow rate via Eq. (3.22) and assuming any carbon not captured was in the form of liquid fallout.

The global combustion equation for a mixed phase (gas and liquid) fuelled flare which may emit unburned liquid fuel is:

$$C_p H_{q(liquid)} + C_x H_{y(gas)} + O_2 = bCO_2 + dH_2O + eCO + fCH_4 + \sum_{m,n} g_{m,n} C_m H_{n(gas)} + hC_{(s)} + jC_p H_{q(liquid)} \quad (3.23)$$

Production rates of all gas species excluding the unburned liquid fuel, $C_p H_q$, can then be defined by Eq. (3.24), which is a modified version of Eq. (3.13), where subscripts FL and FG indicate liquid and gas phases in the flare stream respectively. The production rate of soot can be defined by Eq. (3.21).

$$\begin{aligned} \dot{n}_{i,produced} = & \left((X_{i,plume} - X_{i,\infty}) \dot{n}_{plume,gas} - \{X_{i,FG} \dot{n}_{FG}\}_{inert} \right. \\ & \left. + X_{i,\infty} \frac{1}{M_{\infty}} (M_{FG} \dot{n}_{FG} + M_{C_p H_q,FL} \{\dot{n}_{C_p H_q,FL}\}_{combusted} + M_{tracer} \dot{n}_{tracer}) \right) \end{aligned} \quad (3.24)$$

In Eq. (3.24), $\{\dot{n}_{C_p H_q,FL}\}_{combusted}$ is the portion of the liquid fuel that successfully combusts to produce gas phase products and it is assumed that the mean carbon number and molecular weight of the unburned liquid fuel is the same as that of the liquid fuel in the flare stream. From this derivation of species production rates, the liquid fallout can be quantified using the tracer measured plume flow rate Eq. (3.22) and a carbon balance of the reaction based on Eq. (3.23).

$$\{\dot{n}_{C_p H_q FL}\}_{liquid\ fallout} = \frac{x(X_{C_x H_y FG})\dot{n}_{FG} + p\dot{n}_{C_p H_q FL} + \{X_{CO_2 FG}\dot{n}_{FG}\}_{inert} - \sum_i \#_{C,i} K - \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}} \dot{n}_{plume,gas}}{\left(p - \sum_i \#_{C,i} X_{i,\infty} \frac{M_{C_p H_q FL}}{M_{\infty}}\right)} \quad (3.25)$$

$$\text{where } K = \left[(X_{i,plume} - X_{i,\infty})\dot{n}_{plume,gas} + X_{i,\infty} \left(\frac{M_{FG}}{M_{\infty}} \dot{n}_{FG} + \frac{M_{C_p H_q FL}}{M_{\infty}} \dot{n}_{C_p H_q FL} + \frac{M_{tracer}}{M_{\infty}} \dot{n}_{tracer} \right) \right].$$

3.4 Quantifying Anticipated Uncertainties for a Range of Operating Conditions

The effects of key assumptions were evaluated using synthetic data for which a flare gas composition by volume of 88.01% methane, 7.28% ethane, 3.21% propane and 1.50% butane was assumed. To estimate the achievable uncertainties associated with each method, a range of flare efficiency and dilution scenarios were simulated using typical bias errors for each input variable. To reduce the number of parameters needed to define the product composition of the synthetic data, the form of the emitted product species was fixed as follows: fuel-bound carbon not fully oxidized to CO₂ was emitted as soot (fixed at 0.1% of the fuel-bound carbon), CO (10% of the non- CO₂ gas-phase carbon), and unburned hydrocarbons (90% of non- CO₂ gas-phase carbon, in the same relative volume fractions as the raw fuel). NO_x emissions were fixed at the US EPA (1995) suggested emission factor of 0.068 lb NO_x/10⁶ BTU.

For the purpose of calculating uncertainties, the assumed measurement bias uncertainty on gas species concentrations was the larger of 2% of the measured value or a prescribed detection limit for low concentrations (1.0, 0.5 or 0.1 ppm_v depending on scenario), which is typical of many commercial gas analyzers. The concentration of tracer gas in the plume was held at 50 ppm_v independent of combustion efficiency and dilution ratio. The assumed bias uncertainty on measuring the tracer gas was 2 ppb_v, which is attainable with commercially available modern gas analyzers specifically

tailored for the chosen tracer species. Soot volume fraction was assumed to be measurable with relative bias uncertainty of 20%, and soot density was assumed to be known to a relative bias of 4% or 75.6 kg/m^3 as prescribed by McEwen (2010). The bias used for the flare gas flow rates in the synthetic cases was 1.25% of the individual species flow rate, where the total fuel mass flow bias was the root sum of squares of the bias of the individual fuel species. Bias on the plume temperature and pressure was 2.2 K and 15 Pa respectively.

3.4.1 Anticipated Uncertainties in Measured Combustion Efficiency

The expected uncertainty on measured combustion efficiency was evaluated considering the products of combustion as defined above. Efficiency was calculated based on each of the three methods derived in Sections 3.3.2, 3.3.4, and 3.3.5, and uncertainty was determined using the detailed expressions shown in supplemental material, which were derived in accordance with ANSI/ASME (1985) procedures for estimating uncertainties. The shaded bands in Figure 3.3a represent the range of possible uncertainty for a given detection limit and dilution ratio over the range of uncertainties tested. The uncertainty in measured efficiency increases as the sample becomes more diluted and the concentrations of various species in the plume approach their respective detection limits. The uncertainties calculated for the gas-phase and mixed-phase expressions were negligibly different for the soot production rate tested (0.1% of fuel-bound carbon), as such only the mixed-phase uncertainties are shown below. Additionally, detection limit changes made a negligible difference on the uncertainty of the tracer injection method as CO_2 concentrations were always high enough so that the uncertainty was dictated by assumed 2% bias on the measured value.

Figure 3.3: a) Expected absolute uncertainty on measured combustion efficiency (e.g. 99%±4% equates to a range of 95-103% at a dilution ratio of 200 using the tracer injection method) evaluated with Eq. (3.12) and corresponding supplementary material. Combustion efficiencies greater than 100% are not possible in practice and uncertainties extending beyond this threshold are mathematical artefacts from the uncertainty analysis. b) Expected relative uncertainty on measured species yield (e.g. 1.0 kg/kg ±10% (0.1 kg/kg)) evaluated using Eq. (3.13) with plume flow rate defined by Eq. (3.11) (carbon-balance) and Eq. (3.22) (tracer injection).

3.4.2 Anticipated Uncertainties in Measured Species Emission Rates

The calculation of a species emission rate or species yield (mass production rate normalized by fuel mass flow rate) is dependent on the intermediate calculation of the plume flow rate. Two methods are presented for evaluating the plume flow rate based on either an indirect method utilizing a carbon balance as developed in Section 3.3.2, or using a gaseous tracer injection for direct measurement as developed in Section 3.3.5. The inherent advantage of direct plume measurement is that an instrument with high accuracy specifically targeted to measure the chosen tracer gas will result in a uniform uncertainty across all dilution ratios (for a constant tracer concentration), whereas the uncertainty of the indirect method will increase with dilution ratio. Figure 3.3b plots the relative uncertainties on a general species yield for the two methods at various dilution ratios and species yields. At low yields, the uncertainty grows exponentially as the

concentration measured in the plume approaches the detection limit. Product dilution, as mentioned previously, has an important effect on the uncertainty of the indirect method across the range of species yields. For the direct method, product dilution has little effect at high yields until eventually the uncertainties rise as the measured concentrations of the emitted species being quantified approach the detection limit. Thus, at high species yields and/or low dilution ratios, the achievable relative uncertainty for the tracer injection method is approximately 1.35% lower than the carbon-balance method; at low species yields and/or high dilution ratios, the tracer injection method for quantifying species emissions can maintain this improved uncertainty until species detection limits are reached. In the case of 0.1 ppm_v bias error on the species of interest, the difference between the relative uncertainties of the two methods will increase (for a given yield/dilution ratio) making the tracer injection method preferable for quantifying species yields over this range.

3.5 Demonstration Experiments and Comparison of Methodologies and Uncertainties

Measurements utilizing the methods outlined above were taken in April 2014 at the Carleton University lab-scale flare facility. The facility features a modular burner centered under a large hexagonal exhaust hood (3.4 m included diameter), for which the entrance plane is 3.14 m above the floor beneath the burner. The exhaust hood connects to a 40.6 cm round steel duct which provides exhaust extraction using a variable speed fan capable of drawing ~100,000 SLPM. Sampling is conducted 10.6 m downstream through ports installed in the duct. Samples are drawn through heated sample lines to measurement instruments via vacuum pumps. The flare is operated such that all products

of combustion are collected and diluted, which results in a minimum fixed operational exhaust fan setting for a given fuel mass flow rate. As such the dilution of the products is not directly controlled. Gas-phase analysis is accomplished using a MKS 2030 FTIR instrument which measures up to 20 species of interest simultaneously. Reported bias uncertainties for species of interest measured using the FTIR instrument are 0.15ppm_v, 0.10ppm_v, 0.15ppm_v, 0.30ppm_v, 0.50ppm_v and 0.05ppm_v for CO, CH₄, C₂H₆, C₃H₈, NO and NO₂ respectively. The tracer gas used in the tests presented was acetylene and measurement of the tracer gas was conducted with the same gas analyzer previously mentioned. As such, bias uncertainties on the measured tracer concentration was the greater of 2% or 0.3 ppm_v. Soot volume fraction was continuously measured using an Artium LII 200 instrument, with an estimated bias uncertainty of 20%. Four flare gas mass flow rates ranging from 0.488 to 2.15 g/s were tested on a 38.1 mm-diameter flare tip. The fuel was set to consist of 85.24% methane, 7.06% ethane, 3.11% propane, 1.44% butane, 1.91% carbon dioxide and 1.24% nitrogen, which is consistent with gas flared at battery sites in the upstream energy industry (Johnson and Coderre, 2012). Mass flow controllers were individually calibrated to have bias uncertainties averaging ~1.33% of the set point. The relevant data to be examined in this paper are the uncertainties in measured combustion efficiency, soot yield, and various gas species emission rates. Each flare gas flow rate was tested at the maximum fan speed and exhaust flow rate to produce the highest possible dilution for the tested flaring rates. The numbered designations for each test, as well as the flare gas flow rate and dilution ratio are outlined in Table 3.2.

Table 3.2: Experimental Operating Conditions

Test Number	Flare Gas Flow Rate (grams/second)	Dilution Ratio
1	0.488	216
2	0.878	110
3	1.464	65
4	2.147	40

3.5.1 Combustion Efficiency Measurements and Discussion

Combustion efficiency has been evaluated using the mixed-phase carbon-balance method (Section 3.3.4) and the tracer injection method (Section 3.3.5). The uncertainties on the experimental results as seen in Figure 3.4a reflect the magnitudes suggested by the synthetic data in Figure 3.3a. The high precision of the carbon-balance method results from only trace emissions of non-CO₂ carbon-based species relative to the produced CO₂. The much greater uncertainties of the tracer injection method result from the uncertainty on the measured concentrations of carbon dioxide and tracer gas in the diluted plume.

Figure 3.4: a) Combustion efficiency and uncertainties calculated using derived carbon-balance and tracer injection methods on a 1.5 inch flare over a range of flare gas flow rates. b) NO_x and soot species yields and uncertainties calculated using derived carbon-balance and tracer injection methods on a 1.5 inch flare over a range of flare gas flow rates. Combustion efficiencies greater than 100% are not possible in practice and uncertainties extending beyond this threshold are mathematical artefacts from the uncertainty analysis.

3.5.2 Calculated Species Yields for Various Methods

Species yields and the associated uncertainties have been evaluated for soot and NO_x as plotted in Figure 3.4b. The species yields calculated with the carbon-balance and tracer injection methods agree to within $\sim 5\%$ for a given test case and species. This discrepancy is insignificant compared to the uncertainties on the calculated yields. The relative uncertainty for a given test and species is slightly smaller for the tracer injection method when compared to the carbon-balance method, although the difference is limited by the ability to accurately measure the tracer gas with current instrumentation. The uncertainty in soot yield with either method is dominated by the 20% assumed bias on the measured soot volume fraction. For NO_x , the uncertainty is dominated by low plume concentrations relative to the species detection limit. The decreasing relative uncertainties from Test 1 to Test 4 are a result of decreasing dilution and therefore higher plume concentrations of relevant species. Combustion product dilution ranged from ~ 216 for Test 1 to ~ 40 for Test 4. In the current experiment, all gas species including the tracer gas were measured using the same instrument (MKS 2030 FTIR Gas Analyzer). Future experiments may allow for the use of a device tailored specifically for measurement of the chosen tracer gas (e.g. cavity ring-down gas analyzers are readily available for the tracer (acetylene) used in the current experiment), which will result in reduced uncertainties for the tracer injection method.

3.6 Conclusions

Two complementary analytical approaches were developed for quantifying the combustion efficiency and species emission rates from gas flares represented as turbulent non-premixed flames. The first approach used a carbon-balance to link known flare gas

variables to measureable gas-, or gas- and particulate-phase (soot) carbon emissions. The second method utilized a tracer gas injected into the diluted combustion plume to enable direct relation of measured species concentrations and emission rates. Detailed expressions were derived to enable quantitative evaluation of measurement uncertainties, and the accuracies of the methods were compared alongside other calculations in the literature over a wide range of potential scenarios. Experiments were also performed to further test and validate the derived methods. Analysis of results revealed that the carbon-balance approach generally provides much lower uncertainties when calculating combustion efficiency. However, for species yields, the experimental data suggest that both methods produce similar uncertainties using the current experimental instruments, and significantly improved uncertainties could be expected when using the tracer injection method with a high-precision analyzer specifically suited for measuring the chosen tracer gas.

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Chapter 4

Species Emissions, Combustion Efficiency and Flame Length Results

4.1 Summary of Experiments

Measurement of combustion efficiency along with gas- and solid-phase species emission yields were completed for the test conditions presented in Table 4.1. Results for specific species including soot, NO_x , carbon monoxide and hydrocarbons are presented in Sections 4.2, 4.3, and Appendix B. All species emissions presented in these sections have been calculated using the carbon-balance method as outlined in Section 3.3.4 and are expressed as yields per unit flare gas. Combustion efficiencies calculated using gas-phase species only, and with the inclusion of soot are presented in Section 4.4. The measured flame lengths for a limited number of conditions are presented in Appendix C. Combustion efficiencies and species yields have been measured for three pure flare gases (methane, ethylene and propane) as well as two methane-based flare gas mixtures (AVG 6-Mix and HVY 4-Mix) as defined in Section 2.3 previously. Ethylene and propane tests were performed on a single burner diameter (50.8 mm ID). Methane and AVG 6-Mix tests were performed on two burner diameters (50.8 and 76.2 mm ID) and HVY 4-Mix tests were performed on three burner diameters (38.1, 50.8 and 76.2 mm ID). Exit velocities of the tests ranged from 0.1 to 3.2 m/s calculated at standard exit conditions (273.15 Kelvin and 1 atm). Prior to presentation and discussion of specific results, a

comparison of the carbon-balance and tracer-injection methods for measuring the soot yield is presented in Figure 4.1.

Table 4.1 - Summary of test conditions showing range of fuel mixtures tested at different exit velocity and burner diameter combinations

Burner Diameter (mm)	Target Exit Velocity (m/s)								
	0.1	0.25	0.5	0.8	0.9	1.5	1.85	2.2	3.2
38.1			HVY 4 ^a		HVY 4	HVY 4		HVY 4	HVY 4
50.8	C ₃ H ₈	AVG 6 ^b HVY 4 C ₂ H ₄ C ₃ H ₈	AVG 6 HVY 4 CH ₄ C ₂ H ₄ C ₃ H ₈		AVG 6 HVY 4 CH ₄ C ₂ H ₄ C ₃ H ₈	AVG 6 HVY 4 CH ₄ C ₂ H ₄	HVY 4	AVG 6	
76.2	AVG 6 HVY 4	AVG 6 HVY 4 CH ₄	AVG 6 HVY 4 CH ₄	HVY 4	AVG 6 HVY 4 CH ₄	AVG 6			

^a Heavy 4-Mix flare gas

^b Average 6-Mix flare gas

For a limited number of test cases, measurements were made utilizing acetylene as an injected tracer gas to allow concurrent measurement of the duct flow rate and species emission rates using the tracer-injection method as described in Section 3.3.5. Figure 4.1 presents the soot yields for the Heavy 4-Mix, ethylene, and propane tests calculated using both the tracer-injection and carbon-balance methods. The agreement between the methods was within 11.49% (well within the experimental error bars shown on the figure) for tests with fan settings between 50% and 100% corresponding to duct flow rates between 41,000 and 97,000 ALPM.

Figure 4.1: Comparison of soot yield calculated with the carbon-balance and tracer-injected methods for HVY 4-Mix, ethylene, and propane flare gases.

Experiments at the test conditions outlined in Table 4.1 were performed between one and four times. While ideally all experiments would have been repeated multiple times, this was not possible in practice due to the time and fuel costs to run experiments, especially at the larger flow rate conditions. Thus, precision error cannot be calculated on the subset of experiments performed only once. Additionally, experiments performed only twice would require a large t-value (12.71) for the calculation of precision error. As such, all uncertainties represented in the following sections will represent bias only. To justify this presentation, Figure 4.2 shows the relative uncertainty in terms of bias only and total (precision and bias) uncertainties on measured soot yield for cases where measurements were made either three or four times. Index numbers 1-4 correspond to the test conditions of 0.9 m/s on the 38.1 mm burner, 0.25 and 0.5 m/s on the 50.8 mm burner and 0.25 m/s on the 76.2 mm burner for the HVY 4-Mix flare gas which were each repeated four times each. Index numbers 5-9 correspond to the test conditions of 0.9 and 1.5 m/s on the 50.8 mm burner, 0.1 and 0.5 m/s on the 76.2 mm burner all for the

HVY 6-Mix flare gas, and 0.1 m/s on the 76.2 mm burner for the AVG 6-Mix flare gas, which were each repeated three times each. The relative bias uncertainties on soot yield for these cases ranged from 20.76-21.10% whereas the total relative uncertainties (i.e. including both bias and precision uncertainties) ranged from 23.46-34.02%.

Figure 4.2: Comparison of bias and total (precision and bias) relative uncertainty on measured soot yield for test cases with three and four experimental repeats.

4.2 Soot Yield Results, Analysis and Discussion

Figure 4.3 presents the soot yields calculated using the carbon-balance method for pure methane and the two methane-based flare gas-mixtures. It is apparent from the data that the addition of heavier hydrocarbons (ethane, propane and butane) to a primarily methane-based flare gas dramatically affects the measured soot yield. The average soot yield for all of the AVG 6-Mix flare gas tests is 6.0 times higher than the average soot yield for all of the pure methane test cases. The average soot yield for all HVY 4-Mix tests is an additional 2.4 times higher than the average for all AVG 6-Mix flare gas tests. It is noted at this time that while soot yield does vary with flow rate and burner diameter as evident in Figure 4.3, the effect of either parameter appears less dramatic than changes

in flare gas composition. This is further evidenced in Figure 4.4. The effects of flow rate and burner diameter are separately discussed in Section 4.2.1.

Figure 4.3: Soot yield calculated using the carbon-balance method for the 38.1, 50.8 and 76.2 mm burners with AVG 6-Mix, HVY 4-Mix and methane flare gas mixtures.

Figure 4.4 plots the 50.8 mm burner data for the AVG 6-Mix, HVY 4-Mix and methane flare gases along with the results for ethylene and propane tests also on the 50.8 mm burner. Both ethylene and propane display clear decreasing trends in soot yield as the flare gas mass flow rate is increased. More importantly, both ethylene and propane yield far greater amounts of soot than the methane-based or pure methane flare gases. The average soot yield of all propane tests is 5.6 and 81.4 times higher than the average soot yield of all HVY 4-Mix and all pure methane flare gases respectively, while average soot yields of all ethylene tests are 11.2 and 163.2 times higher respectively. Figure 4.4b displays the soot yields for all flare gases on the 50.8 mm burner on a per flare gas carbon mass basis instead of a per flare gas mass basis in an attempt to collapse the data and account for differences in flare gas chemistry. The flare gases increase in carbon density

from approximately 74 to 86% in the same order as increasing soot yield with the exception of the AVG 6-Mix, which has a lower carbon density than methane due to the presence of diluents. It is clear that the differences in carbon density are not large enough to collapse the differences in soot yields among the different flare gases, which in some cases can range by orders of magnitude.

Figure 4.4: Soot yield on a) per flare gas mass and b) per flare gas carbon mass basis calculated using the carbon balance method for the 50.8 mm burner with AVG 6-Mix, HVY 4-Mix, ethylene, methane and propane flare gas mixtures.

4.2.1 Potential Effects of Varying Flow Regimes

While no observable trends are apparent in the pure methane data, there is a clear decrease in soot yield with increasing flow rate for the HVY 4-Mix tests on the 38.1 mm burner, as seen in Figure 4.3. As noted previously, similar declines in soot yield with increasing flow rate were observed for the ethylene and propane flare gases, as shown in Figure 4.4. Less definite decreases in soot yield are also discernable as the flare gas mass flow rate increases for AVG 6-Mix and HVY 4-Mix tests on the 50.8 mm burner. However, the data for both the AVG 6-Mix and HVY 4-Mix flare gases on the 76.2 mm burner present no clear trend.

As discussed in Section 1.3, Delichatsios (1993) proposed a regime map for non-premixed diffusion flames scaled by Reynolds number (Re) and a Global Fire Froude number (Fr_g) as defined by Eq. (1.1) and Eq. (1.2). Figure 4.5 shows the operating conditions for the current data plotted on the non-dimensional map. The current soot yield data span the “transition buoyant” and “transition shear” regimes defined by the solid diagonal line, as well as the transition from laminar to turbulent pipe flow as defined by the horizontal dashed line (Reynolds number of 4000).

Figure 4.5: Flare exit conditions for 38.1, 50.8 and 76.2 mm burners with AVG 6-Mix, HVY 4-Mix, ethylene, methane and propane flare gas mixtures.

The potential implications of the “transition buoyant” and “transition shear” regime transition as defined by Delichatsios (1993) on measured soot yield are considered in Figure 4.6. To allow comparison on a single plot, the soot yield for each test has been normalized by the maximum soot yield for that respective flare gas and burner diameter combination. Figure 4.6a and Figure 4.6b plot this normalized soot yield against the Fire Froude (Fr_f) and Global Froude (Fr_g) numbers as defined by Eq. (1.3) and Eq. (1.2). Figure 4.6c and Figure 4.6d plot the normalized soot yield against Reynolds number and a parameter ($Re \cdot Fr_g^2$) resulting from the definition of the solid diagonal transition line defined in Figure 4.5. The dashed vertical line in Figure 4.6c represents the transition from laminar to turbulent pipe flow ($Re = 4000$) and the solid vertical line in Figure 4.6d represents the transition-buoyant to transition-shear regime transition (Delichatsios, 1993) in terms of $Re \cdot Fr_g^2$. Plotted against any of the parameters represented in Figure 4.6, it is clear that the normalized soot yield for many flare gas and burner diameter combinations generally decreases as Fire Froude number, Global Froude

number, Reynolds number, and the $Re \cdot Fr_g^2$ parameter are increased for a given flare gas and burner diameter combination.

Figure 4.6: Soot yield normalized by the maximum yield for a given flare gas and burner diameter plotted against the a) Fire and b) Global Froude numbers, as well as c) Reynolds number and d) a Reynolds-Global Froude parameter for 38.1, 50.8 and 76.2 mm burners with AVG 6-Mix, HVY 4-Mix, ethylene, methane and propane flare gas mixtures. Possible transition lines of ($Re = 4000$) and ($Re \cdot Fr_g^2 = 1.46$) shown in c) and d) as dashed and solid vertical lines respectively.

Figure 4.7 examines more closely the transition points for Reynolds number and the $Re \cdot Fr_g^2$ parameter shown in Figure 4.6c and Figure 4.6d respectively. Figure 4.7a and Figure 4.7b separate the normalized soot yields at a Reynolds number value of 4000. Whereas the data in Figure 4.7a display no clear trend, in Figure 4.7b there are decreases in the soot yield for all flare gas species and burner diameters as Reynolds number increases. Figure 4.7b does not include pure methane flare gas cases as only a single test condition for each burner diameter exceeded a Reynolds number of 4000. Similarly, Figure 4.7c and Figure 4.7d separate the data at the transition point of $Re \cdot Fr_g^2 = 1.46$. Again there is a mix of increases, decreases and general flatness in the normalized soot yields for values less than 1.46 as shown in Figure 4.7c, whereas all test conditions for $Re \cdot Fr_g^2$ values greater than 1.46 display decreases in soot yield as the $Re \cdot Fr_g^2$ parameter increases. Only single test conditions for the HVY 4-Mix flare gas on the 76.2 mm burner, pure methane on the 76.2 and 50.8 mm burners and propane on the 50.8 mm burner exceeded a $Re \cdot Fr_g^2$ value of 1.46, thus these data do not appear in Figure 4.7d.

Figure 4.7: Soot yield normalized by the maximum yield for a given flare gas and burner diameter plotted against Reynolds numbers a) less than and b) greater than 4000, as well as Reynolds-Global Froude parameter values c) less than and d) greater than 1.46 for 38.1, 50.8 and 76.2 mm burners with AVG 6-Mix, HVY 4-Mix, ethylene, methane and propane flare gas mixtures.

4.2.2 Scaling of Soot Emissions with Heating Value

Certain particulate matter emission factors in the literature (e.g. the CAPP recommended emission factor for NPRI reporting outlined in Section 1.2.1, Table 1.1) attempt to

account for varying flare gas compositions by scaling single-valued factors according to the heating value of the flare gas. As explained by McEwen and Johnson (McEwen and Johnson, 2012),

“The CAPP guide instead gives a value of 2.5632 kg soot per 10³ m³ of fuel and notes that the US EPA value has been “corrected” for a gas with a heating value of 45 MJ/m³. The CAPP guide does not specify how this apparent factor of 3 correction was derived, although it likely resulted from an assumed linear scaling of soot emission with heating value, since landfill gas could be expected to have a heating value on the order of 15 MJ/m³, and a heating value of 45 MJ/m³ should be typical of flare gas in the UOG industry.”

Figure 4.8a investigates the appropriateness of scaling soot yield data with heating value based on the present measured data for varying flare gas compositions. The data suggest that scaling soot yield by volumetric heating value may be valid for the pure alkane (methane and propane) and alkane-based flare gas mixtures (AVG 6-Mix and HVY 4-Mix) tested, however it is not at all valid when flare gases with other chemical structures, such as the alkene ethylene, are considered.

McEwen (2010) suggested that for measured soot yield data of alkane flare gas mixtures on flares 38.1 mm or greater in diameter, and with Fire Froude numbers greater than 0.003, the soot yield may scale simply with heating value. These criteria were suggested based on available data implying a soot yield plateauing beyond this threshold, although the limitations of the experimental facility used by McEwen (2010) precluded testing in this range. The current experimental facility permitted higher flare gas flow rates on the 50.8 and 76.2 mm diameter flares than the experiments of McEwen (2010). In contrast to the supposition of McEwen (2010), the current soot yield data as plotted against Fire Froude number in Figure 4.6a suggest that soot yield generally decreases

with increasing Fire Froude number beyond a value of 0.003 after having previously reached a maximum.

Figure 4.8b displays the maximum soot yield for each burner diameter tested on alkane flare gases from the current work along with a linear fit to these data. Selecting the maximum soot yield for a given burner and flare gas combination presents an upper bound on the soot yield which can then be applied across a range of volumetric heating values. This suggested upper bound for soot yield scaled with the flare gas volumetric heating value is compared to the fit suggested by McEwen (McEwen, 2010). The linear scaling from that work was fit for data on 38.1, 50.8 and 76.2 mm diameter burners with Fire Froude numbers greater than 0.003 and with volumetric heating values of 38-47 MJ/m³. The current data not only extends the range of volumetric heating values over which there is soot yield data for alkane flare gases available but also suggests that the increase of soot yield with respect to volumetric heating value may be steeper than previously shown.

Figure 4.8: Soot yield calculated using the carbon balance method and plotted against volumetric heating value (HV) for (a) AVG 6-Mix, HVY 4-Mix, ethylene, methane and propane flare gases and 38.1, 50.8 and 76.2 mm burners; and (b) the maximum soot yield for a flare gas and burner diameter combination for alkane-based flare gases (AVG 6-Mix, HVY 4-Mix, methane and propane) and 38.1, 50.8 and 76.2 mm burners. Panel (c) is a zoomed image of panel (b) to better illustrate the correlation with the data for the methane-based flare gases only.

4.2.3 Comparison of present Soot Yield data with Current Emission Factors

Figure 4.9 superimposes various particulate matter emission factors from the literature (see Section 1.2.1) on the soot yield data from the 50.8 mm diameter burner for all flare gases tested. In Figure 4.9a, the range of current soot emission factors is presented as the shaded grey region, where the upper limit of the range corresponds to the AP 42 Section 13.5 value of 0.0034 kg/kg-flare-gas for the “heavily smoking” case, and the lower limit of 0 kg/kg-flare-gas corresponds to the AP 42 Section 13.5 “non-smoking” case. It is clear that the range of soot emission factors after being converted to soot yield on a mass basis extends only as high as the minimum soot yield measured for the propane flare gas, while falling well below the soot yields measured for the ethylene flare gas. The conversion of emission factors to common yield units expressed per mass of flare gas was accomplished assuming a standard flare gas density of 0.85 kg/m^3 except in the case of the AP 42 Section 13.5 data (which is presented in terms of measured plume concentrations). The emission factors reported in AP 42 Section 13.5 were converted following the procedure outlined in McEwen (2010) with corrections for a flare gas composition of crude propylene (80% propylene and 20% propane) in lieu of 100% propylene. The various smoke levels attributed to this source have been converted from per volume to per mass basis based on the density of crude propylene at standard conditions. As suggested by McEwen (2010), these factors represent a minimum soot yield for the smoking conditions as dilution of the sample was unknown and an undiluted sample was assumed.

Figure 4.9b shows the various emission factors along with data for the pure methane, pure propane, and methane-based flare gas mixtures. It is interesting that many

currently available emission factors (i.e. AP 42 Section 13.5 “heavily smoking” and “average smoking”, CAPP, ARPEL Sweet/Sour/Steam-Assisted, EEA, Villasenor) lie in the region between the methane-based and pure-propane flare gases. This may suggest that these emission factors were based on flare gas compositions containing more heavy hydrocarbons than the methane-based flare gases of the current work. However, the difference in the case of the AP 42 emission factors, the values also reflect necessary assumptions to convert concentration-based emission factors into yield units. The lower cluster of emission factors (WebFIRE, NAEI, AP 42 Section 13.5 “light smoking”, AP 42 Section 2.4) which are presented for methane, upstream gas production related flaring, light smoking crude propylene, and landfill waste gas respectively present values that are in line with the measured soot yields for the AVG 6-Mix and HVY 4-Mix flare gases which range from ~74% to ~85% methane by volume.

Of particular interest is the CAPP emission factor, which is suggested for use in the Alberta upstream oil and gas industry for flare gases with a nominal heating value of 45 MJ/m³. When converted to a per mass basis as specified in Table 1.1 and shown in Figure 4.9b, the CAPP factor predicts a soot yield value much higher than those measured in the current work for methane-based flare gases with heating values in the range of 39-51 MJ/m³. This suggests that the derivation of the CAPP factor from the confidential US EPA (1991) report and the application of this factor to flares in the upstream energy industry with nominal heating value of 45 MJ/m³ is questionable.

Figure 4.9: Soot yield calculated using the carbon balance method for the 50.8 mm burner with AVG 6-Mix, HVY 4-Mix, ethylene, methane and propane flare gas mixtures showing a) a shaded area encompassing the range of soot emission factors and b) with specific emission factors from the literature.

4.3 NO_x Yield Results, Analysis and Discussion

The measured NO_x yields for all flare gases and burner diameters are presented in Figure 4.10a,b,c on a per flare gas mass, volume, and energy content basis. The data suggest that NO_x has a relatively constant yield for a given flare gas irrespective of burner diameter or the flare gas mass flow rate, which follows the idea that formation of NO_x is primarily driven by the flame temperature. The NO_x yield evaluated per unit mass of flare gas as shown in Figure 4.10a, or per unit energy content of flare gas adjusted by the higher heating value as shown in Figure 4.10c, collapse the data for different flare gases into a narrow range of yield values (1.36-2.34 g-NO_x/kg-flare-gas and 26.7-45.9 g-NO_x/10⁹ J-flare gas). Evaluating the NO_x yield on a per volume basis adjusted for the

density of the flare gas as in Figure 4.10b expands the range of yield values (1.05-3.15 kg/10³ m³-flare-gas) and suggests that yields evaluated on this basis will vary depending on the chemistry of the flare gas. Thus, emission factors presented on a per flare gas volume basis such as the CAPP factor will be valid only for a limited range of specific flare gases.

Linear curve fits were applied to the data in Figure 4.10, which all show a very slight positive correlation between the different forms of NO_x yield represented and increasing flare gas mass flow rate ($r^2=0.053$, 0.002, 0.093 for the fits in Figure 4.10a, b and c respectively). Assuming that there is actually no correlation between NO_x yield and flare gas mass flow rate, the variance (σ^2) of the data multiplied by the number of data points (n) and normalized by the mean ($mean$) squared would indicate which form of the NO_x yield has the least scatter in the data. The values for $n\sigma^2/mean^2$ for the data in Figure 4.10 are 0.410, 3.400 and 0.314 for NO_x yield calculated on a per mass, per volume and per energy content basis respectively. This indicates that the largest scatter occurs when NO_x yields are plotted on a per volume basis (Figure 4.10b, $n\sigma^2/mean^2=3.4$) and that a single valued emission factor would be best expressed as a NO_x yield on a per energy content basis best (Figure 4.10c, $n\sigma^2/mean^2=0.314$).

Figure 4.10 also includes the relevant NO_x emission factors available from the literature as previously detailed in Table 1.2. The emission factors have been adjusted to SI units where necessary, but are otherwise presented in their original form in the relevant panel (a-c) of Figure 4.10 on either a per mass, per volume, or per energy content basis (e.g. AP 42 Section 13.5 EF of 0.068 lb/10⁶ BTU flare gas is presented on a per energy content basis in Figure 4.10c converted to SI units of kg/10⁹ J). This avoids

the necessity of assuming a specific flare gas density or heating value when converting a given emission factor to a single common yield form (e.g. kg-NO_x/kg-flare-gas). Figure 4.10a includes emission factors calculated for gas flaring in crude oil and gas treatment (Shah and Pope, 1994), for flaring specifically related to oil and gas extraction (Trozzi, 2013), and for upstream oil or gas production related flaring (NAEI, 2012). These emission factors from the literature and presented on a per unit mass of flare gas basis fall below the average NO_x yield of 0.00198 kg/kg calculated from the current data. Figure 4.10b presents emission factors for sour gas flares (Villasenor et al., 2003), solution gas combustion at heavy crude primary and thermal facilities (Franklin and Leahey, 1998), for flared gas in the upstream oil and gas industry (CAPP, 2007), and for landfill gas flares (US EPA, 1998; US EPA, 2014). The first three emission factors are similar to the measured yields for the methane-based flare gases and significantly lower than the ethylene and propane yields. The final two are for low energy content gases and produce values much lower than experimentally measured yields for all flare gases. Figure 4.10c shows emission factors for steam-assisted flaring (Franklin and Leahey, 1998) and for industrial flares (US EPA, 1995), which are significantly higher and slightly lower respectively than the average NO_x yield of 0.0376 kg/10⁹ J calculated from the current data.

Figure 4.10: NO_x yields on a per flare gas a) mass, b) volume and c) energy content basis calculated using the carbon balance method plotted against flare gas mass flow rate for the 38.1, 50.8 and 76.2 mm burners with AVG 6-Mix, HVY 4-Mix, ethylene, methane and propane flare gas mixtures. Emission factors from the literature also plotted in their published form as per appropriate reference.

4.3.1 Scaling of NO_x Emissions

As described in Section 1.3, Rokke et al. (1992) proposed a simple scaling relation for NO_x yield from hydrocarbon flare gases, which relates a parameterized NO_x emissions index to the Froude number (Eq. (1.4)) of the flare gas. Figure 4.11a shows the current data plotted in terms of these variables with a superimposed line representing the specific fit values of the scaling law proposed by Rokke et al. (1992) (44 as the coefficient, 0.6 as the exponent). Both axes on the plot are functions of exit velocity (u_0) and burner diameter (d_0) and consequently, if the exponent value on the Froude number were 0.5, then the NO_x yield would be independent of Froude number (and therefore exit velocity and flare gas flow rate). As shown in Figure 4.11a, the current data generally confirm the trend of the theoretical scaling relation from the literature, but the near constant yields observed in Figure 4.10 imply an exponent on the Froude number closer to 0.5. If the NO_x emissions index is expressed on a per mass basis as in Figure 4.11b, the data collapses due to differences in flare gas densities and a curve fit on the current data confirms that the NO_x scaling has a weaker dependence on Froude number (and therefore exit velocity) than the dependence suggested by the Rokke et al. (1992) scaling law. Figure 4.11c replicates the form of Figure 4.11b, but with linear axis to better illustrate the curve fit through the data.

Figure 4.11: NO_x Emission Index a) by volume and b) by mass plotted against Froude number for 38.1, 50.8 and 76.2 mm burners with AVG 6-Mix, HVY 4-Mix, ethylene, methane and propane flare gas mixtures. Also shown: a) theoretical scaling law of $Y_{NO_x} \left[\frac{\rho_0 u_0}{d_0} \right] = 44 \cdot Fr^{0.6}$ (Rokke et al., 1992); b) curve fit of $Y_{NO_x} \left[\frac{u_0}{d_0} \right] = 26.15 \cdot Fr^{0.559}$; c) data and curve fit of b) with linear axis scaling.

Although the equation for the curve fit shown in both Figure 4.11b and c shows good correlation between the NO_x emission index expressed on a mass basis and the Froude number ($r^2=0.984$), the effectiveness of this correlation is misleading given the presence of a u_0/d_0 term in both axes. Figure 4.12 instead shows the NO_x yield on a per mass basis as a function of $Fr^{0.559}$ multiplied by d_0/u_0 (i.e. rewriting the yield as a function of velocity and diameter using the equation from the curve in Figure 4.11c).

Both the gravity term in the denominator of the Froude number and the coefficient on the curve fit can be ignored as they will scale all data points equally and not affect the relative scatter. By plotting the data in accordance with the curve fit in Figure 4.11, a linear fit can be applied between NO_x yield and the velocity parameter ($u_0^{0.117}d_0^{0.441}$) as shown in Figure 4.12. The plotted results illustrate that the resultant curve fit has a very weak correlation with a r^2 value of 0.087. The scatter of the data about the fit (calculated as the residual sum of squares (RSS) divided by the average of the y-axis values (*mean*) squared) is higher ($\text{RSS}/\text{mean}^2 = 0.375$) than the scatter achieved when the NO_x yield per energy content of the flare gas is treated as a constant (which has a comparable $n\sigma^2/\text{mean}^2$ value of 0.314). This shows that the apparent good correlation in Figure 4.11 is primarily an artefact of having u_0/d_0 terms on both axes, and ultimately reflects the trivial truth that emission rate (as opposed to emission yield) scales with flow rate.

Figure 4.12: NO_x yields calculated on a mass basis using the carbon balance method for the 38.1, 50.8 and 76.2 mm burners with AVG 6-Mix, HVY 4-Mix, ethylene, methane and propane flare gas mixtures plotted against the velocity parameter adapted from Froude number scaling.

Given the importance of the thermal mechanism in production of NO_x at high temperatures associated with combustion (Turns, 1995), the stoichiometric, adiabatic flame temperature (T_{ad}) for the individual flare gases was investigated as a potential scaling parameter, as shown in Figure 4.13. Figure 4.13a plots NO_x yield as a function of T_{ad} and Figure 4.13b plots the NO_x yield multiplied by the stoichiometric mixture fraction (f_s) as a function T_{ad} . Multiplying the NO_x yield by f_s results in a parameter which considers the mass of NO_x produced per mass of hot products rather than per mass of flare gas. In Figure 4.13a, the yields for methane are on average the highest followed by ethylene and the HVY 4-Mix which suggests weak positive correlation ($r^2=0.023$) with increasing adiabatic flame temperature. In Figure 4.13b, ethylene now presents the highest average parameterized yield while propane has also increased relative to the methane-based flare gases. The NO_x yields parameterized with stoichiometric mixture fraction result in adiabatic flame temperature scaling with a stronger (but still weak) positive correlation ($r^2=0.274$) compared to the adiabatic flame temperature alone. An explanation for the absence of NO_x yield scaling with respect to the adiabatic flame temperature alone is that the heat losses due to radiation from to the production of soot in the flame lower the flame temperature relative to T_{ad} . For the flare gases tested, the soot yield increases in the same order as adiabatic flame temperature and stoichiometric mixture fraction.

Figure 4.13: a) NO_x yield and b) NO_x yield multiplied by the stoichiometric mixture fraction, f_s , calculated using the carbon balance method plotted against adiabatic flame temperature for the 38.1, 50.8 and 76.2 mm burners with AVG 6-Mix, HVY 4-Mix, ethylene, methane and propane flare gas mixtures.

4.3.2 Recommendations for Estimating NO_x Emissions from Flares

Given that NO_x yield expressed on a per energy basis gives the least scatter in the measured data, a final comparison with all emission factors from Table 1.2 is shown in Figure 4.14 on a per unit flare gas energy content basis. As discussed previously, a curve fit on the data results in a very weak upward trend ($r^2=0.093$) relating NO_x yield and increasing flare gas flow rate.

Figure 4.14: NO_x yields calculated using the carbon balance method for the 38.1, 50.8 and 76.2 mm burners with AVG 6-Mix, HVY 4-Mix, ethylene, methane and propane flare gas mixtures compared to emission factors from the literature.

Several conclusions can be drawn from the investigation into NO_x yields and their potential scaling. The available data suggest that a single-value NO_x emission factor is best presented on a per energy content basis (adjusted for flare heating value) as this provides the least scatter independent of flare gas chemistry. Based on the present experiments as plotted in Figure 4.14, the average NO_x yield calculated on a per flare gas energy content basis is 0.0376 kg-NO_x/10⁹ J-flare-gas. Although the fit to these data increases very slightly with flare gas flow rate, if the data for the lower flow rates with high uncertainties are neglected the slope of the curve fit approaches zero making a single-value emission factor a good approximation for NO_x yield.

The average value presented for the data in Figure 4.14 compares well to the cluster of emission factors (ARPEL solution gas, Villasenor, CAPP, AP 42 Section 13.5, E&P Forum, EEA and NAEI) that fall in the range of 0.0264 to 0.0356 kg-NO_x/10⁹ J-flare-gas after being converted to common units. Plotting the emission factors in Figure 4.14 required various assumptions that should be reemphasized. Of the factors

mentioned, only AP 42 Section 13.5 is published in the form of mass yield per unit energy content. The emission factors from ARPEL specifically for solution gas (Franklin and Leahey, 1998), Villasenor et al. (2003) (for sour gas), and CAPP (2007) (for upstream oil and gas flares) are published in the form of mass yield per unit volume and have been converted to the relevant units assuming a volumetric heating value of 45 MJ/m^3 , which is in the middle of the range of methane flare gases tested ($39\text{--}51 \text{ MJ/m}^3$). The emission factors from E&P Forum (Shah and Pope, 1994), EEA (Trozzi, 2013) and NAEI (2012) (all for solution gas) are published in the form of mass yield per unit mass and have been converted to the relevant units assuming a higher heating value of 45 MJ/m^3 and density of 0.85 kg/m^3 .

The three outlier emission factors relative to the cluster of emission factors within the range of the current data are the ARPEL factor for steam-assisted flaring (Franklin and Leahey, 1998), the AP 42 factor (US EPA, 1998) for enclosed flares burning presumably methane, and the WebFIRE factor (US EPA, 2014) for landfill gas flaring. The validity of these factors applied to upstream oil and gas flaring is questionable because steam-assisted flaring is a fundamentally different combustion process as are enclosed flares, and landfill gas generally has high diluent content and low heating values ($\sim 15 \text{ MJ/m}^3$) which may lead to lower flame temperatures and reduced NO_x yield.

4.4 Combustion Efficiency Results, Analysis and Discussion

The combustion efficiencies of turbulent diffusion flames were measured for the test conditions outlined in Table 1.1. It was expected based on a review of the literature that, for the range of conditions tested (i.e. higher heating value flare gases and an absence of crosswind), the results would exhibit high combustion efficiencies. As shown in Figure

4.15, the mixed-phase combustion efficiencies measured were consistently high (> ~98%) for all but one test condition. The lone test case with measured combustion efficiency less than 98% was the lowest flow rate for ethylene which also resulted in the highest soot yield of all tests. For flares burning the methane-based mixtures (AVG 6-Mix, HVY 4-Mix, and pure methane), the combustion efficiencies were greater than 99.5% for all cases except the lowest flow rate test condition for AVG 6-Mix with the 76.2 mm burner. The relatively low measured combustion efficiency of 98.7% for this case was an artifact of abnormally high concentrations of ethane measured in the duct. It is believed this test case should be regarded as an experimental outlier and is likely not indicative of reduced combustion efficiency in general at this flow rate for this flare gas. There was no discernable impact on combustion efficiency with changes in the burner diameter for any of the three methane-based flare gases. The heavier flare gases (ethylene, propane), which resulted in increased soot yields relative to the methane-based flare gases, showed a corresponding decrease in combustion efficiency. The general increase in combustion efficiency with increasing mass flow rate apparent in all flare gas mixtures can for the most part be attributed to decreasing soot yield with increasing mass flow rates. This trend of increasing combustion efficiency is particularly apparent in ethylene and propane while still observable in the methane-based flare gases.

Figure 4.15: Mixed-phase combustion efficiency calculated using the carbon balance method for the 38.1, 50.8 and 76.2 mm burners with AVG 6-Mix, HVY 4-Mix, ethylene, methane and propane flare gas mixtures.

To illustrate the importance of soot as a product of incomplete combustion, individual carbon-based species yields are shown in Figure 4.16 for the various flare gases and burner diameters. The individual bars for a given burner diameter and flare gas composition set correspond to increases in flare gas mass flow rate from left to right. This figure illustrates two important points. For ethylene and propane flare gases, the carbon monoxide yield is of roughly the same magnitude as the total carbon yield for the AVG 6-Mix, HVY 4-Mix, and pure methane flare gases. However, the soot yield dominates the total carbon yield of both ethylene and propane. The previously mentioned outlier case of a high ethane measurement for the AVG 6-Mix with the 76.2 mm burner that resulted in decreased combustion efficiency can be seen in the right-most bar grouping. The carbon monoxide and hydrocarbon yields for methane, ethane, propane and ethylene can be found in Appendix B.

Figure 4.16: Carbon yields of various species calculated using the carbon balance method for the 38.1, 50.8 and 76.2 mm burners with AVG 6-Mix, HVY 4-Mix, ethylene (EY), methane (ME) and propane (PR) flare gas mixtures.

Figure 4.17 compares the gas-phase-only combustion efficiencies neglecting the impact of soot as a product of incomplete combustion. The gas-phase only combustion efficiency considers carbon monoxide and gaseous hydrocarbons (methane, ethane, propane, ethylene) as products of incomplete combustion. The results as shown illustrate the small change in combustion efficiency for the methane-based flare gases due to their relatively low soot yield and already high mixed-phase combustion efficiencies. The gas-phase combustion efficiencies of the ethylene and propane flare gases are higher than their corresponding mixed-phase combustion efficiencies and are close to the gas phase efficiencies of the methane-based gases. This suggests that independent of the specific flare gas, gas-phase combustion efficiencies are universally high for turbulent non-premixed diffusion flames operating with high heating values and in the absence of crosswinds.

Figure 4.17: Gas-phase only combustion efficiency calculated using the carbon balance method for the 38.1, 50.8 and 76.2 mm burners with AVG 6-Mix, HVY 4-Mix, ethylene, methane and propane flare gas mixtures.

Chapter 5

Conclusions & Recommendations

5.1 Conclusions

Mass emission yields of soot, NO_x and several carbon-based species were measured along with combustion efficiency for several pure flare gases and two methane-based flare gas mixtures representative of compositions flared in the Alberta upstream oil and gas industry. To facilitate these measurements, a large lab-scale flare was constructed and commissioned, significantly expanding the range of experiments possible in previous work of McEwen (2010) and Canteenwalla (2007) which used a smaller facility. A new sampling protocol and calculation methodology were developed to leverage capabilities of modern high-sensitivity gas analysis equipment and enable measurements on larger flames at higher flow rates and dilution ratios. The resulting calculation methodology and uncertainty analysis procedures were published in a paper co-authored by the author of this thesis, which detailed two complementary approaches for measuring flare combustion efficiency and gas species emission rates with quantified uncertainties.

Experiments were subsequently performed on a range of flare diameters, flow rates, and flare gas compositions. Results of soot yield measurements affirmed that yield rates are most strongly influenced by flare gas chemistry, and flare gas flow rates and diameters are of secondary importance. Soot yields measured with methane-based flare gases peaked at 0.00134 kg-soot/kg-flare-gas with the HVY 4-Mix flare gas

(74.54% CH₄, 15.47% C₂H₆, 6.83% C₃H₈ and 3.16% C₄H₁₀ by volume). However among the three methane-based flare gases, there was more than an order of magnitude difference in soot yield between flares burning the average HVY 4-Mix soot yield and pure methane. Both propane and ethylene produced significantly more soot than the methane-based flare gases, averaging 0.00597 and 0.0120 kg-soot/kg-flare-gas respectively.

The secondary effects of varying flare gas flow rate and burner diameter were investigated through scaling by non-dimensional parameters including the Fire Froude number, Global Froude number, and Reynolds number. In this context, it appears that the transitional regimes for turbulent buoyant non-premixed flames suggested by Delichatsios (1993) may correspond with decreasing soot yields in the transition-shear regime. Changes in the burner diameter for a given flare gas appear to influence soot yield less strongly than the flare gas flow rate.

The measured soot yields were compared to a number of published emission factors for various forms of gas flaring. Several of the emission factor values lie in the range of measured soot yield for the methane-based flare gases, and the remainder lie in the range between measured soot yields for methane-based and propane flare gases. An investigation into the validity of heating value scaling (which is inherently assumed in several emission factors) was undertaken. The CAPP (2007) emission factor is derived from an emission factor cited in US EPA (2014) using linear scaling with assumed heating values. The measured soot yields suggest this method may be applicable for the narrow range alkane based flare gases tested; however it is certainly not valid for the

ethylene flare gas. It seems likely that the presence of alkenes or other non-alkane species in the flare gas would invalidate this scaling approach.

Measured NO_x yields were generally constant over the range of flare gas flow rates tested for a given flare gas chemistry. Efforts were made to examine on which basis yield should be expressed to reduce the scatter among different flare gases. The proposed theoretical scaling of Rokke et al. (1992) for parameterized NO_x yield as a function of Froude number was compared to the measured data and results confirmed that NO_x yield can likely be expressed as a constant independent of flare gas flow rate. Analysis revealed that the scaling relation proposed by (Rokke et al., 1992) based on this parameterized NO_x yield is partly an artefact of having u_o/d_o terms on both axes, and the correlation simplifies to a weak scaling of mass yield with $u_o^{0.2}$. The scatter among this revised correlation was actually worse than the scatter observed when yield was expressed on a per flare gas energy content basis. The potential of scaling with the adiabatic flame temperature was also investigated for NO_x yield on a mass basis parameterized by the stoichiometric mixture fraction, although the weak correlation could be attributed to the strong correlation between stoichiometric mixture fraction and adiabatic flame temperature.

Results of the present investigation into NO_x scaling suggest NO_x yield expressed on a per energy content basis ($\text{kg}/10^9 \text{ J}$) is approximately constant over the range of conditions tested, with an average NO_x yield of $0.0376 \text{ kg}/10^9 \text{ J}$. Measured NO_x data expressed on a per energy content basis were compared with several published emission factors. Most of the available emission factors aligned with the present range of measured NO_x yields when a representative heating value and density were used for the

conversion to common units. Outlying published emission factors were either significantly higher (ARPEL factor for steam-assisted flaring), or significantly lower (US EPA factors for enclosed flares and landfill gas flaring).

Combustion efficiencies were also measured with and without the inclusion of soot in the calculations. The mixed-phase (with soot) combustion efficiencies decreased among the flare gases in accordance with increasing soot yield to a minimum of 97.8% for the ethylene flare gas. Gas-phase (without soot) combustion efficiencies were consistently high (>99.5%), highlighting the fact that soot was the most significant carbon-based product of incomplete combustion accounting for up to 90% of non-CO₂ carbon species.

5.2 Recommendations for Future Work

Several recommendations are suggested for future experiments to expand the current work. In general, the understanding of soot and NO_x yields could be better understood with an expanded testing campaign specifically including propane and ethylene flare gas tests conducted on the 38.1 and 76.2 mm burners to confirm the expectation that burner diameter is not a leading order scaling parameter. Expansion of the range of flare gases tested to include other alkene species (possibly propylene) and alkane-alkene blends may be useful to further investigate emissions scaling among alkenes. Measurement of parameters such as the radiant fraction or a thorough examination of the literature on the soot propensity of the various flare gases may present opportunities for inter-species collapse of the soot yield data. Additionally, Laser Doppler Velocimetry (LDV) measurements of turbulence in the exit plane and along the length of the flame to investigate mixing may help better explain the influence of flare gas flow rate on soot

yield. Further testing on different flare gases and at higher flare gas mass flow rates (and by association higher Froude numbers) would aid in confirming or refuting the suggestion that NO_x yield presented on a per energy content basis is independent of flare gas chemistry and flow rate. This would allow for a more robust recommendation to be made as to an emission factor valid for a wide range of flare gas compositions and flow rates. Measurement of the flame temperature, while difficult to accomplish in sooting turbulent flames, would present a better opportunity for scaling given the importance of temperature in NO_x production. Radiant heat transfer from soot particles tends to reduce the temperature from the adiabatic temperature considered in the current analysis.

Improved gas-analysis equipment with lower minimum detection limits would be beneficial in reducing the uncertainties of measured gas-species yields. For carbon-based species, this would reduce the uncertainties associated with combustion efficiency (although uncertainties would still be heavily dependent on the ability to measure CO_2 better than a relative bias of $\pm 2\%$). For NO_x yield, this would allow for a more precise examination of potential differences among gas species as well as provide more definitive evidence whether yield is truly independent of flow rate. Finally, the current work considered quiescent conditions, which are expected to represent an upper bound on both soot and NO_x production. Future experiments to measure the yields of these species for flames subjected to turbulent crosswind (i.e. in a large-scale windtunnel) would provide important insight for conditions experienced by flares in the field.

References

- Allen, D.T. and Torres, V.M., (2011). TCEQ 2010 Flare Study Final Report. PGA No. 582-8-862-45-FY09-04, Austin, TX, Texas Commission on Environmental Quality (TCEQ). Available at: <http://www.tceq.texas.gov/assets/public/implementation/air/rules/Flare/2010flarestudy/2010-flare-study-final-report.pdf>
- ANSI/ASME, (1985). ANSI/ASME PTC 19.1 - Part 1 – Measurement Uncertainty, Instruments and Apparatus. New York, NY, United States.
- Arctic Council, (2011). Arctic Council Task Force on Short-Lived Climate Forcers Progress Report and Recommendations for Ministers, Nuuk Greenland. Arctic Council Task Force on Short-Lived Climate Forcers. Available at: http://arctic-council.npolar.no/accms/export/sites/default/en/meetings/2011-nuuk-ministerial/docs/3-0a_TF_SPM_recommendations_2May11_final.pdf
- Bakken, J., Langørgen, Ø., Husdal, G., and Henriksen, T.S., (2008). *Improving Accuracy in Calculating NO_x Emissions from Gas Flaring*. In SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, April 15-17. Nice, France, Society of Petroleum Engineers, p.SPE 111561.
- Bandaru, R. V and Turns, S.R., (2000). Turbulent Jet Flames in a Crossflow: Effects of Some Jet, Crossflow, and Pilot-Flame Parameters on Emissions. *Combust. Flame*. 121:137–151.
- Becker, H.A. and Liang, D., (1982). Total emission of soot and thermal radiation by free turbulent diffusion flames. *Combust. Flame*. 44:305–318.
- Bond, T.C., Doherty, S.J., Fahey, D.W., Forster, P.M., Berntsen, T., DeAngelo, B.J., Flanner, M.G., Ghan, S., Kärcher, B., Koch, D., et al., (2013). Bounding the role of black carbon in the climate system: A scientific assessment. *J. Geophys. Res. Atmos.*. 118:5380–5552.
- Bourguignon, E., Johnson, M.R., and Kostiuk, L.W., (1999). The use of a closed-loop wind tunnel for measuring the combustion efficiency of flames in a cross flow. *Combust. Flame*. 119:319–334.
- Canteenwalla, P.M., (2007). Soot emissions from turbulent diffusion flames burning simple alkane fuels. Carleton University, Ottawa, ON, Canada.

- CAPP, (2007). A Recommended Approach to Completing the National Pollutant Release Inventory (NPRI) for the Upstream Oil and Gas Industry. 2007-0009, Available at: <http://www.capp.ca/library/publications/policyRegulatory/pages/pubInfo.aspx?DocId=119572#a3C7EUiuVHbf>
- Caulton, D.R., Shepson, P.B., Cambaliza, M.O.L., McCabe, D., Baum, E., and Stirm, B.H., (2014). Methane destruction efficiency of natural gas flares associated with shale formation wells. *Environ. Sci. Technol.*. 48:9548–54.
- Costa, M., Parente, C., and Santos, A., (2004). Nitrogen oxides emissions from buoyancy and momentum controlled turbulent methane jet diffusion flames. *Exp. Therm. Fluid Sci.*. 28:729–734.
- Crosland, B.M., Thomson, K.A., and Johnson, M.R., (2014). *Simultaneous Instantaneous Measurements of Soot Volume Fraction, Primary Particle Diameter, and Aggregate Size in Turbulent Buoyant Diffusion Flames*. In 35th International Symposium on Combustion.
- Delichatsios, M.A., (1993). Transition from momentum to buoyancy-controlled turbulent jet diffusion flames and flame height relationships. *Combust. Flame*. 92:349–364.
- Ellzey, J.L., Berbe, J.G., Tay, E.Z.F., and Foster, D.E., (1990). Total Soot Yield from a Propane Diffusion Flame in Cross-Flow. *Combust. Sci. Technol.*. 71:41–52.
- Franklin, N. and Leahey, D.M., (1998). Atmospheric Emissions Inventories Methodologies in the Petroleum Industry.
- Grahame, T.J., Klemm, R., and Schlesinger, R.B., (2014). Public health and components of particulate matter: The changing assessment of black carbon. *J. Air Waste Manage. Assoc.*. 64:620–660.
- Havs, P.T.I.L., (2012). Veiledning til den Årlige Utslippsrapporteringen. . 1–99.
- Herndon, S.C., Nelson, D.D., Wood, E.C., Knighton, W.B., Kolb, C.E., Kodesh, Z., Torres, V.M., and Allen, D.T., (2012). Application of the Carbon Balance Method to Flare Emissions Characteristics. *Ind. Eng. Chem. Res.*. 51:12577–12585.
- IPCC, (2013). Working Group I Contribution to the IPCC 5th Assessment Report “Climate Change 2013: The Physical Science Basis” - Final Draft Underlying Scientific-Technical Assessment. Geneva, Switzerland, Intergovernmental Panel on Climate Change (IPCC). Available at: www.ipcc.ch
- Johnson, M.R. and Coderre, A.R., (2012). Compositions and greenhouse gas emission factors of flared and vented gas in the western Canadian sedimentary basin. *J. Air Waste Manage. Assoc.*. 62:992–1002.

- Johnson, M.R., Devillers, R.W., and Thomson, K.A., (2011). Quantitative Field Measurement of Soot Emission from a Large Gas Flare Using Sky-LOSA. *Environ. Sci. Technol.* 45:345–350.
- Johnson, M.R., Devillers, R.W., and Thomson, K.A., (2013). A Generalized Sky-LOSA Method to Quantify Soot/Black Carbon Emission Rates in Atmospheric Plumes of Gas Flares. *Aerosol Sci. Technol.* 47:1017–1029.
- Johnson, M.R., Devillers, R.W., Yang, C., and Thomson, K.A., (2010). Sky-Scattered Solar Radiation Based Plume Transmissivity Measurement to Quantify Soot Emissions from Flares. *Environ. Sci. Technol.* 44:8196–8202.
- Johnson, M.R. and Kostiuk, L.W., (2000). Efficiencies of low-momentum jet diffusion flames in crosswinds. *Combust. Flame*. 123:189–200.
- Johnson, M.R. and Kostiuk, L.W., (2002). A parametric model for the efficiency of a flare in crosswind. *Proc. Combust. Inst.* 29:1943–1950.
- Johnson, M.R., Kostiuk, L.W., and Spangelo, J.L., (2001). A characterization of solution gas flaring in Alberta. *J. Air Waste Manage. Assoc.* 51:1167–1177.
- Johnson, M.R., Wilson, D.J., and Kostiuk, L.W., (2001). A fuel stripping mechanism for wake-stabilized jet diffusion flames in crossflow. *Combust. Sci. Technol.* 169:155–174.
- Kostiuk, L.W., Majeski, A.J., Poudenx, P., Johnson, M.R., and Wilson, D.J., (2000). Scaling of wake-stabilized jet diffusion flames in a transverse air stream. *Proc. Combust. Inst.* 28:553–559.
- McDaniel, M., (1983). Flare efficiency study. EPA-600/2-83-052, Research Triangle Park, NC, United States Environmental Protection Agency. Available at: <http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockkey=P1003QGZ.txt>
- McEwen, J.D.N., (2010). Soot Emission Factors from Lab-Scale Flares Burning Solution Gas Mixtures. (*M.A.Sc. Thesis*). Carleton University, Ottawa, ON, Canada.
- McEwen, J.D.N. and Johnson, M.R., (2012). Black Carbon Particulate Matter Emission Factors for Buoyancy Driven Associated Gas Flares. *J. Air Waste Manage. Assoc.* 62:307–321.
- Myhre, G., Shindell, D., Bréon, F.-M., Collins, W., Fuglestad, J., Huang, J., Koch, D., Lamarque, J.-F., Lee, D., Mendoza, B., et al., (2013). *Anthropogenic and Natural Radiative Forcing*. In T. F. Stocker, D. Qin, G.-K. Plattner, M. Tignor, S. K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex, & P. M. Midgley, eds. *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge,

- United Kingdom and New York, NY, USA, Cambridge University Press, pp.659–740.
- NAEI, (2012). Emission factors detailed by source and fuel.
<http://naei.defra.gov.uk/data/data-selector>
- NGDC, (2014). Global/Country Results 1994 - 2010.
http://www.ngdc.noaa.gov/eog/interest/gas_flares.html
- OLF Environmental Programme, (1991). Report Phase I, Part A, Emissions to Air.
- Pohl, J.H., Lee, J., Payne, R., and Tichenor, B.A., (1986). Combustion efficiency of flares. *Combust. Sci. Technol.* 50:217–231.
- Poudenx, P., (2000). Plume sampling of a flare in crosswind: structure and combustion efficiency. (*M.Sc. Thesis*). Edmonton, University of Alberta, Edmonton, AB, Canada.
- Rokke, N.A., Hustad, J.E., Sonju, O.K., and Williams, F.A., (1992). Scaling of Nitric Oxide Emissions from Buoyancy-Dominated Hydrocarbon Turbulent-Jet Diffusion Flames. *Proc. Combust. Inst.* 24:385–393.
- Santos, A. and Costa, M., (2005). Reexamination of the scaling laws for NO_x emissions from hydrocarbon turbulent jet diffusion flames. *Combust. Flame*. 142:160–169.
- Shah, A. and Pope, P., (1994). Methods for Estimating Atmospheric Emissions from E&P Operations. 2.59/197, London, UK, The Oil Industry International Exploration & Production Forum. Available at: <http://www.epforum.org>
- Sivathanu, Y.R. and Faeth, G.M., (1990). Soot volume fractions in the overfire region of turbulent diffusion flames. *Combust. Flame*. 81:133–149.
- Stohl, A., Klimont, Z., Eckhardt, S., Kupiainen, K., Shevchenko, V.P., Kopeikin, V.M., and Novigatsky, A.N., (2013). Black carbon in the Arctic: the underestimated role of gas flaring and residential combustion emissions. *Atmos. Chem. Phys.* 13:8833–8855.
- Stroscher, M.T., (2000). Characterization of emissions from diffusion flare systems. *Journal of the Air & Waste Management Association*, 50(10) pp.1723–33
- Talebi, A., Fatehifar, E., Alizadeh, R., and Kahforoushan, D., (2014). The Estimation and Evaluation of New CO, CO₂, and NO_x Emission Factors for Gas Flares Using Pilot Scale Flare. *Energy Sources, Part A Recover. Util. Environ. Eff.* 36:719–726.

- Torres, V.M., Herndon, S., and Allen, D.T., (2012). Industrial Flare Performance at Low Flow Conditions. 2. Steam- and Air-Assisted Flares. *Ind. Eng. Chem. Res.*. 51:12569–12576.
- Torres, V.M., Herndon, S., Kodesh, Z., and Allen, D.T., (2012). Industrial Flare Performance at Low Flow Conditions. 1. Study Overview. *Ind. Eng. Chem. Res.*. 51:12559–12568.
- Torres, V.M., Herndon, S., Wood, E., Al-Fadhli, F.M., and Allen, D.T., (2012). Emissions of Nitrogen Oxides from Flares Operating at Low Flow Conditions. *Ind. Eng. Chem. Res.*. 51:12600–12605.
- Trozzi, C., (2013). 1.B.2.c Venting and flaring. . 1–15.
- Turns, S., (1995). Understanding NO_x formation in nonpremixed flames: Experiments and modeling. *Prog. Energy Combust. Sci.*. 21:361–385.
- UKOOA, (1993). Methods for Estimating Atmospheric Emissions from UK Oil and Gas Exploration and Production Facilities in the UK Continental Shelf Area.
- US EPA, (1991). Data from landfill gas flare, Confidential Report No. ERC-55.
- US EPA, (1995). AP 42 - Compilation of Air Pollutant Emission Factors, Volume I, 5th ed. - Section 13.5 Industrial Flares. AP-42, Research Triangle Park, NC, U.S. Environmental Protection Agency (US EPA). Available at: <http://www.epa.gov/ttn/chief/ap42/ch13/index.html>
- US EPA, (1998). AP 42 - Compilation of Air Pollutant Emission Factors, Volume I, 5th ed. - Section 2.4 Municipal Solid Waste Landfills. AP-42, Research Triangle Park, NC, U.S. Environmental Protection Agency (US EPA). Available at: <http://www.epa.gov/ttn/chief/ap42/ch02/index.html>
- US EPA, (2004). Air Quality Criteria for Particulate Matter Volume I. Research Triangle Park, NC.
- US EPA, (2012). Report to Congress on Black Carbon. EPA-450/R-12-001, Research Triangle Park, NC, United States Environmental Protection Agency.
- US EPA, (2013a). Carbon Monoxide - National Trends in CO Levels. <http://www.epa.gov/airtrends/carbon.html#conat>
- US EPA, (2013b). Atmospheric Concentrations of Greenhouse Gases. http://www.epa.gov/climatechange/pdfs/print_ghg-concentrations-2013.pdf
- US EPA, (2014). WebFIRE. <http://cfpub.epa.gov/webfire/>

Villasenor, R., Magdaleno, M., Quintanar, A., Gallardo, J., Lopez, M., Jurado, R., Miranda, A., Aguilar, M., Melgarejo, L., Palmerin, E., et al., (2003). An air quality emission inventory of offshore operations for the exploration and production of petroleum by the Mexican oil industry. *Atmos. Environ.* 37:3713–3729.

Appendix A Supplemental Information for Calculating Uncertainty on Combustion Efficiency, Plume Flow Rate, Species Emissions Rates, and Destruction Removal Efficiency

Detailed Expressions and Methodologies for Measuring Flare Combustion Efficiency, Species Emission Rates, and Associated Uncertainties

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Calculating Uncertainty on Combustion Efficiency, Plume Flow Rate, Species Emission Rates, and Destruction Removal Efficiency

An uncertainty analysis based on the ANSI/ASME (1985) standard is outlined for the combustion efficiency, plume flow rate, species emission rate, and destruction removal efficiency (DRE) expressions developed in the manuscript. Uncertainty on a measurement is defined as the root sum of squares of the systematic and precision errors. By determining the sources of possible systematic error in a measured quantity, a set of expressions can be developed to evaluate the sensitivity of that quantity to its input variables. The systematic error of each input variable is assumed to be normally distributed. This error is generally determined by the equipment used to measure the

input variable and does not vary among measurements in a given experimental setup. The systematic error of a function, B_f , is defined in Eq. (A.1) as the square root of the summed squared product of the sensitivity indices, $\theta_{f,i}$, and the systematic errors, B_{x_i} , of each contributing measured variable, x_i :

$$B_f = \left(\sum_{i=1}^n [\theta_{f,i} B_{x_i}]^2 \right)^{1/2} \quad (\text{A.1})$$

Precision error, P , is determined from repeated measurements at the same conditions using the same experimental set up, and is defined generally by Eq. (A.2) using the 95% confidence interval student t-value:

$$P = t_{v,95\%} \frac{\sigma}{\sqrt{N}} \quad (\text{A.2})$$

where σ is the sample standard deviation and N is the sample size. The degrees of freedom, v , for determining the student t -value is calculated as $N - 1$. Systematic and precision error defined by Eq. (A.1) and Eq. (A.2) above are combined in quadrature to determine the total uncertainty on a set of measurements via Eq. (A.3).

$$U = \sqrt{B_f^2 + P^2} \quad (\text{A.3})$$

The sensitivity index, $\theta_{f,i}$, for a measured variable x_i is the partial derivative of the output function with respect to that variable:

$$\theta_{f,i} = \frac{\partial f}{\partial x_i} \quad (\text{A.4})$$

The various expressions for combustion efficiency, plume flow rate, species emission rate, and DRE presented in the manuscript have explicit partial derivatives for each measured variable. Table A1 presents a list of these measured variables alongside

typical values of their component errors for the Carleton lab-scale flare experimental set up. These values would be subject to adjustment depending on instrumentation used.

Table A1: Variables appearing in sensitivity indices of combustion efficiency, plume gas flow rate, and species emission rate functions

i	Variable, x_i	Definition	Typical Systematic Error Value, B_{x_i}
1	x	carbon coefficient of fuel hydrocarbons	~0.3% of carbon coefficient
2	$X_{C_xH_y,FG}$	hydrocarbon volume fraction in fuel	~2.5% of flare gas C_xH_y fraction
3	$X_{CO_2,FG}$	carbon dioxide diluent volume fraction in fuel	~2.5% of flare gas CO_2 fraction
4	$X_{CO_2,plume}$	plume carbon dioxide volume fraction	2% of measured concentration
5	$X_{CO_2,\infty}$	ambient carbon dioxide volume fraction	2% of measured concentration
6	$X_{CO,plume}$	plume carbon monoxide volume fraction	0.15 ppm _v detection limit
7	$X_{CO,\infty}$	ambient carbon monoxide volume fraction	0.15 ppm _v detection limit
8	$X_{CH_4,plume}$	plume methane volume fraction	0.10 ppm _v detection limit
9	$X_{CH_4,\infty}$	ambient methane volume fraction	0.10 ppm _v detection limit
10	$X_{C_mH_n,plume}$	plume non-methane hydrocarbon volume fraction	0.30 ppm _v detection limit
11	$X_{C_mH_n,\infty}$	ambient non-methane hydrocarbon volume fraction	0.30 ppm _v detection limit
12	$f_{v,measured}$	plume soot volume fraction	20% of measured soot volume fraction
13	T_{sample}	soot volume fraction sample measurement temperature	2.2 Kelvin
14	P_{plume}	absolute pressure of plume	15 Pascals
15	M_{FG}	molar mass of flare gas	~1.7% of flare gas molar mass
16	$\dot{m}_{FG}$	mass flow rate of flare gas	~1.2% of flare gas mass flow rate
17	$\dot{m}_{tracer}$	mass flow rate of tracer gas	~1.27% of tracer gas mass flow rate
18	X_{tracer}	plume tracer volume fraction with injection	2% of measured concentration
19	X_{tracer}^*	plume tracer volume fraction prior to injection	0.30 ppm _v detection limit
20	$\dot{n}_{plume,gas}$	molar flow rate of diluted combustion plume	
21	$X_{i,plume}$	plume volume fraction of species i	species dependant
22	$X_{i,\infty}$	ambient volume fraction of species i	species dependant
23	$X_{i,FG}$	diluent volume fraction in fuel of species i	species dependant

Multiple explicit expressions were developed for combustion efficiency and plume flow rate as outlined in the manuscript. Eq. (3.19) and Eq. (3.12) define combustion efficiency using the carbon-balance method with and without the inclusion of black carbon measurement respectively. Plume flow rate is also defined for the carbon-

balance method with and without measurement of black carbon, Eq. (3.17) and Eq. (3.11), as well as for the tracer-injection method, Eq. (3.22). The sensitivity indices presented in the following sections are derived for the more general case including black carbon measurement. For cases where only gas phase measurements are considered, i.e. Eq. (3.12) and Eq. (3.13), terms including the measured soot volume fraction, $f_{v,measured}$, should be set to zero along with $\theta_{f,12}$ through $\theta_{f,14}$ in Table A2 and Table A3.

A1 Sensitivity Indices for Combustion Efficiency Calculated Via the Carbon-Balance Method

The combustion efficiency calculated using the carbon-balance method, including a black carbon measurement, is defined per Eq. (3.19) in the manuscript as:

$$\eta[\%] = \frac{x(X_{C_xH_y,FG})B - X_{CO_2,FG}F + (X_{CO_2,\infty}G - X_{CO_2,plume}(X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,C_mH_n} X_{C_mH_n,\infty})) \frac{M_{FG}}{M_{\infty}}}{x(X_{C_xH_y,FG})(X_{CO_2,plume} - X_{CO_2,\infty} + F)} \times 100 \quad (3.19)$$

where $B = (X_{CO_2,plume} - X_{CO_2,\infty})$,

$$F = ((X_{CO,plume} - X_{CO,\infty} + X_{CH_4,plume} - X_{CH_4,\infty} + \sum_{m,n} \#_{C,C_mH_n} (X_{C_mH_n,plume} - X_{C_mH_n,\infty})) + H),$$

$$G = (X_{CO,plume} + X_{CH_4,plume} + \sum_i \#_{C,C_mH_n} X_{C_mH_n,plume} + H), \text{ and}$$

$$H = \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}}.$$

The sensitivity indices for evaluating systematic error on combustion efficiency are given in Table A2 below. The numbered sensitivity indices in Table A2 correspond to the variable numbers defined in Table A1, and indicate the variable of differentiation used to develop the expression. As noted previously, if black carbon is neglected the measured soot volume fraction (contained in the coefficient D) and indices $\theta_{\eta,12}$ through $\theta_{\eta,14}$ should be set equal to zero.

Table A2: Sensitivity indices for combustion efficiency, η

$\theta_{\eta,1} = \frac{X_{CO_2,FG}F - (X_{CO_2,\infty}G - X_{CO_2,plume}(X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,CmHn} X_{CmHn,\infty})) \frac{M_{FG}}{M_{\infty}}}{x^2(X_{C_xH_y,FG})(X_{CO_2,plume} - X_{CO_2,\infty} + F)} \times 100$
$\theta_{\eta,2} = \frac{X_{CO_2,FG}F - (X_{CO_2,\infty}G - X_{CO_2,plume}(X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,CmHn} X_{CmHn,\infty})) \frac{M_{FG}}{M_{\infty}}}{x(X_{C_xH_y,FG})^2(X_{CO_2,plume} - X_{CO_2,\infty} + F)} \times 100$
$\theta_{\eta,3} = -\frac{(X_{CO,plume} - X_{CO,\infty} + X_{CH_4,plume} - X_{CH_4,\infty} + \sum_{m,n} \#_{C,CmHn}(X_{CmHn,plume} - X_{CmHn,\infty}) + H)}{x(X_{C_xH_y,FG})(X_{CO_2,plume} - X_{CO_2,\infty} + F)} \times 100$
$\theta_{\eta,4} = \frac{(x(X_{C_xH_y,FG}) + X_{CO_2,FG} - (X_{CO_2,\infty} + X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,CmHn} X_{CmHn,\infty})) \frac{M_{FG}}{M_{\infty}} F}{x(X_{C_xH_y,FG})(X_{CO_2,plume} - X_{CO_2,\infty} + F)^2} \times 100$
$\theta_{\eta,5} = -\frac{(x(X_{C_xH_y,FG}) + X_{CO_2,FG} - (X_{CO_2,plume} + X_{CO,plume} + X_{CH_4,plume} + \sum_i \#_{C,CmHn} X_{CmHn,plume} + H)) \frac{M_{FG}}{M_{\infty}} F}{x(X_{C_xH_y,FG})(X_{CO_2,plume} - X_{CO_2,\infty} + F)^2} \times 100$
$\theta_{\eta,6} = \theta_{\eta,8} = \frac{\theta_{\eta,10}}{\#_{C,CmHn}} = -\frac{(x(X_{C_xH_y,FG}) + X_{CO_2,FG} - (X_{CO_2,\infty} + X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,CmHn} X_{CmHn,\infty})) \frac{M_{FG}}{M_{\infty}} B}{x(X_{C_xH_y,FG})(X_{CO_2,plume} - X_{CO_2,\infty} + F)^2} \times 100$
$\theta_{\eta,7} = \theta_{\eta,9} = \frac{\theta_{\eta,11}}{\#_{C,CmHn}} = \frac{(x(X_{C_xH_y,FG}) + X_{CO_2,FG} - (X_{CO_2,plume} + X_{CO,plume} + X_{CH_4,plume} + \sum_i \#_{C,CmHn} X_{CmHn,plume} + H)) \frac{M_{FG}}{M_{\infty}} B}{x(X_{C_xH_y,FG})(X_{CO_2,plume} - X_{CO_2,\infty} + F)^2} \times 100$
$\theta_{\eta,12} = -\frac{H}{f_{v,measured}} \left(\frac{(x(X_{C_xH_y,FG}) + X_{CO_2,FG} - (X_{CO_2,\infty} + X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,CmHn} X_{CmHn,\infty})) \frac{M_{FG}}{M_{\infty}} B}{x(X_{C_xH_y,FG})(X_{CO_2,plume} - X_{CO_2,\infty} + F)^2} \right) \times 100$
$\theta_{\eta,13} = -\frac{H}{T_{sample}} \left(\frac{(x(X_{C_xH_y,FG}) + X_{CO_2,FG} - (X_{CO_2,\infty} + X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,CmHn} X_{CmHn,\infty})) \frac{M_{FG}}{M_{\infty}} B}{x(X_{C_xH_y,FG})(X_{CO_2,plume} - X_{CO_2,\infty} + F)^2} \right) \times 100$
$\theta_{\eta,14} = \frac{H}{P_{plume}} \left(\frac{(x(X_{C_xH_y,FG}) + X_{CO_2,FG} - (X_{CO_2,\infty} + X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,CmHn} X_{CmHn,\infty})) \frac{M_{FG}}{M_{\infty}} B}{x(X_{C_xH_y,FG})(X_{CO_2,plume} - X_{CO_2,\infty} + F)^2} \right) \times 100$
$\theta_{\eta,15} = \frac{(X_{CO_2,\infty}G - X_{CO_2,plume}(X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,CmHn} X_{CmHn,\infty}))}{M_{\infty}x(X_{C_xH_y,FG})(X_{CO_2,plume} - X_{CO_2,\infty} + F)} \times 100$

The systematic error on combustion efficiency calculated using the carbon-balance method can now be evaluated with Eq. (A.5) using the sensitivity index expressions from Table A2 and appropriate component systematic error values (such as those specified in Table A1):

$$B_{\eta} = \left(\sum_{i=1}^{15} [\theta_{\eta,i} B_{x_i}]^2 \right)^{1/2} \quad (A.5)$$

This systematic error ((A.5)) can then be combined in quadrature with the experimental precision error (Eq. (A.2)) to determine the total uncertainty on a set of measurements in accordance with Eq. (A.3).

A2 Sensitivity Indices for Plume Flow Rate Determined using the Carbon-Balance Method

The plume flow rate, $\dot{n}_{plume,gas}$, calculated using the carbon-balance method including black carbon measurement is defined per Eq. (3.17) in the manuscript. By incorporating the substitution from Eq. (3.18), $\dot{n}_{plume,gas}$ may be written as:

$$\dot{n}_{plume,gas} = \frac{x(X_{C_xH_y,FG})\frac{\dot{m}_{FG}}{M_{FG}} + X_{CO_2,FG}\frac{\dot{m}_{FG}}{M_{FG}} - (X_{CO_2,\infty} + X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,C_mH_n} X_{C_mH_n,\infty})\frac{\dot{m}_{FG}}{M_{\infty}}}{X_{CO_2,plume} - X_{CO_2,\infty} + \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}} + A} \quad (A.6)$$

where $A = (X_{CO,plume} - X_{CO,\infty} + X_{CH_4,plume} - X_{CH_4,\infty} + \sum_{m,n} \#_{C,C_mH_n} (X_{C_mH_n,plume} - X_{C_mH_n,\infty}))$, and

$$D = (X_{CO,plume} + X_{CH_4,plume} + \sum_i \#_{C,C_mH_n} X_{C_mH_n,plume})$$

The sensitivity indices for evaluating the systematic error on $\dot{n}_{plume,gas}$ calculated with the carbon-balance method are shown in Table A3 below. Similar to the calculation of systematic error for combustion efficiency, if black carbon is not measured the term $f_{v,measured}$ and indices $\theta_{\dot{n}_{plume,gas},12}$ through $\theta_{\dot{n}_{plume,gas},14}$ should be set equal to zero.

Table A3: Sensitivity indices for plume flow rate, $\dot{n}_{plume,gas}$

$\theta_{\dot{n}_{plume,gas},1} = \frac{X_{C_xH_y,FG} \frac{\dot{m}_{FG}}{M_{FG}}}{X_{CO_2,plume} - X_{CO_2,\infty} + \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}} + A}$
$\theta_{\dot{n}_{plume,gas},2} = \frac{\frac{\dot{m}_{FG}}{M_{FG}}}{X_{CO_2,plume} - X_{CO_2,\infty} + \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}} + A}$
$\theta_{\dot{n}_{plume,gas},3} = \frac{\frac{\dot{m}_{FG}}{M_{FG}}}{X_{CO_2,plume} - X_{CO_2,\infty} + \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}} + A}$
$\theta_{\dot{n}_{plume,gas},4} = \theta_{\dot{n}_{plume,gas},6} = \theta_{\dot{n}_{plume,gas},8} = \frac{\theta_{\dot{n}_{plume,gas},10}}{\#_{C,CmHn}} = - \frac{x(X_{C_xH_y,FG}) \frac{\dot{m}_{FG}}{M_{FG}} + X_{CO_2,FG} \frac{\dot{m}_{FG}}{M_{FG}} - (X_{CO_2,\infty} + X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,CmHn} X_{CmHn,\infty}) \frac{\dot{m}_{FG}}{M_{\infty}}}{\left(X_{CO_2,plume} - X_{CO_2,\infty} + \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}} + A \right)^2}$
$\theta_{\dot{n}_{plume,gas},5} = \theta_{\dot{n}_{plume,gas},7} = \theta_{\dot{n}_{plume,gas},9} = \frac{\theta_{\dot{n}_{plume,gas},11}}{\#_{C,CmHn}} = \frac{x(X_{C_xH_y,FG}) \frac{\dot{m}_{FG}}{M_{FG}} + X_{CO_2,FG} \frac{\dot{m}_{FG}}{M_{FG}} - \left(X_{CO_2,plume} + D + \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}} \right) \frac{\dot{m}_{FG}}{M_{\infty}}}{\left(X_{CO_2,plume} - X_{CO_2,\infty} + \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}} + A \right)^2}$
$\theta_{\dot{n}_{plume,gas},12} = - \frac{\rho_{C(s)} R_u T_{sample}}{M_{C(s)} P_{plume}} \left(\frac{x(X_{C_xH_y,FG}) \frac{\dot{m}_{FG}}{M_{FG}} + X_{CO_2,FG} \frac{\dot{m}_{FG}}{M_{FG}} - (X_{CO_2,\infty} + X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,CmHn} X_{CmHn,\infty}) \frac{\dot{m}_{FG}}{M_{\infty}}}{\left(X_{CO_2,plume} - X_{CO_2,\infty} + \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}} + A \right)^2} \right)$
$\theta_{\dot{n}_{plume,gas},13} = - \frac{\rho_{C(s)} f_{v,measured} R_u}{M_{C(s)} P_{plume}} \left(\frac{x(X_{C_xH_y,FG}) \frac{\dot{m}_{FG}}{M_{FG}} + X_{CO_2,FG} \frac{\dot{m}_{FG}}{M_{FG}} - (X_{CO_2,\infty} + X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,CmHn} X_{CmHn,\infty}) \frac{\dot{m}_{FG}}{M_{\infty}}}{\left(X_{CO_2,plume} - X_{CO_2,\infty} + \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}} + A \right)^2} \right)$
$\theta_{\dot{n}_{plume,gas},14} = \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} (P_{plume})^2} \left(\frac{x(X_{C_xH_y,FG}) \frac{\dot{m}_{FG}}{M_{FG}} + X_{CO_2,FG} \frac{\dot{m}_{FG}}{M_{FG}} - (X_{CO_2,\infty} + X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,CmHn} X_{CmHn,\infty}) \frac{\dot{m}_{FG}}{M_{\infty}}}{\left(X_{CO_2,plume} - X_{CO_2,\infty} + \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}} + A \right)^2} \right)$
$\theta_{\dot{n}_{plume,gas},15} = - \left(\frac{x(X_{C_xH_y,FG}) \frac{\dot{m}_{FG}}{M_{FG}} + X_{CO_2,FG} \frac{\dot{m}_{FG}}{M_{FG}}}{M_{FG}^2} \left(X_{CO_2,plume} - X_{CO_2,\infty} + \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}} + A \right) \right)$
$\theta_{\dot{n}_{plume,gas},16} = \frac{\frac{x(X_{C_xH_y,FG})}{M_{FG}} + \frac{X_{CO_2,FG}}{M_{FG}} - (X_{CO_2,\infty} + X_{CO,\infty} + X_{CH_4,\infty} + \sum_i \#_{C,CmHn} X_{CmHn,\infty}) \frac{\dot{m}_{FG}}{M_{\infty}}}{\left(X_{CO_2,plume} - X_{CO_2,\infty} + \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{M_{C(s)} P_{plume}} + A \right)}$

The systematic error on $\dot{n}_{plume,gas}$ calculated using the carbon-balance method can now be evaluated with Eq. (A.7) using the sensitivity indices provided in Table A3 in combination with appropriate component bias error values (such as those specified in Table A1):

$$B_{\dot{n}_{plume,gas}} = \left(\sum_{i=1}^{16} \left[\theta_{\dot{n}_{plume,gas},i} B_{x_i} \right]^2 \right)^{1/2} \quad (A.7)$$

This systematic error (Eq. (A.7)) can then be combined in quadrature with the experimental precision error (Eq. (A.2)) to determine the total uncertainty on a set of measurements in accordance with Eq. (A.3).

A3 Sensitivity Indices for Plume Flow Rate using Tracer Gas Measurement

For a measurement of $\dot{n}_{plume,gas}$ using the tracer-injection method, Eq. (3.22) from the manuscript is used:

$$\dot{n}_{plume,gas} = \frac{\dot{m}_{tracer}(1 - X_{tracer}^*)}{(X_{tracer} - X_{tracer}^*)} \quad (4.X)$$

Calculation of $\dot{n}_{plume,gas}$ via the tracer-injection method utilizes a different set of variables than those used in the carbon-balance method. These appear as variables 17 through 19 in Table A1 alongside typical values of their systematic errors. The corresponding sensitivity indices for calculating the systematic error on $\dot{n}_{plume,gas}$ determined via the tracer-injection method are given in Table A4.

Table A4: Sensitivity indices for plume flow rate measurement using tracer gas, $\dot{n}_{plume,gas}$

$\theta_{\dot{n}_{plume,gas},17} = \frac{\frac{1}{\dot{m}_{tracer}}(1 - X_{tracer}^*)}{(X_{tracer} - X_{tracer}^*)}$
$\theta_{\dot{n}_{plume,gas},18} = -\frac{\frac{\dot{m}_{tracer}(1 - X_{tracer}^*)}{\dot{m}_{tracer}}}{(X_{tracer} - X_{tracer}^*)^2}$
$\theta_{\dot{n}_{plume,gas},19} = \frac{\frac{\dot{m}_{tracer}(1 - X_{tracer})}{\dot{m}_{tracer}}}{(X_{tracer} - X_{tracer}^*)^2}$

The systematic error on $\dot{n}_{plume,gas}$ calculated using the tracer-injection method can now be determined with Eq. (A.8) using the sensitivity indices from Table A4 and appropriate component systematic error values (such as those specified in Table A1).

$$B_{\dot{n}_{plume,gas}} = \left(\sum_{i=17}^{19} [\theta_{\dot{n}_{plume,gas},i} B_{x_i}]^2 \right)^{1/2} \quad (A.8)$$

This systematic error (Eq. (A.8)) can then be combined in quadrature with the experimental precision error (Eq. (A.2)) to determine the total uncertainty on a set of measurements in accordance with Eq. (A.3).

A4 Sensitivity Indices for Species Emission Rates and Destruction Removal Efficiency

All species emission rates and DREs are functions of the general intermediate variable, $\dot{n}_{plume,gas}$, which can be calculated using either the carbon-balance, Eq. (3.11) or Eq. (3.17), or the tracer-injection method, Eq. (3.22). General expressions derived in the manuscript for the mass production rate of a gas species i , Eq. (3.13), and black carbon as soot, Eq. (3.21), are reprinted below. A generalized expression for DRE is defined by Eq. (A.9). The specific sensitivity indices used to calculate systematic error on a species emission rate or DRE are not identical between the carbon-balance and tracer-injection methods in all instances. When calculating the emission rate of a carbon-based species (either gas-phase carbon-based species or black carbon) or DRE of a carbon-based species present in the flare gas using the carbon-balance method, the uncertainty analysis is complicated by a lack of independence between the species of interest and the calculated plume flow rate. This is addressed in Section A4.2. Section A4.1 details the procedure for calculating uncertainties in any species emission rate or DRE determined via the tracer-injection method, and for non-carbon-based species emission rates DRE determined via the carbon-balance method.

$$\dot{m}_{i,produced} = M_i \left((X_{i,plume} - X_{i,\infty}) \dot{n}_{plume,gas} - \left\{ X_{i,FG} \frac{\dot{m}_{FG}}{M_{FG}} \right\}_{inert} + X_{i,\infty} \frac{\dot{m}_{FG}}{M_{\infty}} \right) \quad (3.13)$$

$$\dot{m}_{C(s),produced} = \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{P_{plume}} \dot{n}_{plume,gas} \quad (3.21)$$

$$DRE_i [\%] = \left(1 - \frac{(X_{i,plume} - X_{i,\infty}) \dot{n}_{plume,gas} + X_{i,\infty} \frac{\dot{m}_{FG}}{M_{\infty}}}{X_{i,FG} \frac{\dot{m}_{FG}}{M_{FG}}} \right) \times 100 \quad (A.9)$$

A4.1 Sensitivity Indices for Species Emission Rates and DREs Determined using the Tracer-Injection Method and for Non-Carbon-Based Gas-Phase Species Emission Rates and DREs Determined using the Carbon-Balance Method

The equations in this section are used to calculate the systematic error in any species emission rate or DRE determined via the tracer-injection method, and the systematic error in any non-carbon-based species emission rate (e.g. NO_x) or DRE (e.g. H₂S) determined via the carbon-balance method. The sensitivity indices for these cases are given in Table A5 (gas-phase emission rate), Table A6 (black carbon emission rate) and Table A7 (DRE). The indices include the sensitivity to the flare gas molar mass, $\theta_{f,15}$, and mass flow rate, $\theta_{f,16}$, as well as several unique indices. $\theta_{f,20}$ refers to the plume flow rate systematic error as calculated using Eq. (A.7) or Eq. (A.8), and $\theta_{f,21}$ through $\theta_{f,23}$ refer to the specific gas species for which the emission rate or DRE is being quantified.

Table A5: Sensitivity indices for gas species emission rate, $\dot{m}_{i,produced}$ (used for calculation of systematic error in any species emission rate determined via the tracer-injection method and for calculation of systematic error in any non-carbon-based species emission rate determined via the carbon-balance method)

$\theta_{\dot{m}_{i,produced},15} = M_i \left\{ X_{i,FG} \frac{\dot{m}_{FG}}{M_{FG}^2} \right\}_{inert}$
$\theta_{\dot{m}_{i,produced},16} = M_i \left(\frac{X_{i,\infty}}{M_{\infty}} - \left\{ \frac{X_{i,FG}}{M_{FG}} \right\}_{inert} \right)$
$\theta_{\dot{m}_{i,produced},20} = M_i (X_{i,plume} - X_{i,\infty})$
$\theta_{\dot{m}_{i,produced},21} = M_i \dot{n}_{plume,gas}$
$\theta_{\dot{m}_{i,produced},22} = M_i \left(\frac{\dot{m}_{FG}}{M_{\infty}} - \dot{n}_{plume,gas} \right)$
$\theta_{\dot{m}_{i,produced},23} = -M_i \frac{\dot{m}_{FG}}{M_{FG}}$

Table A6: Sensitivity indices for soot emission rate, $\dot{m}_{C(s),produced}$ (used for calculation of systematic error in black carbon emission rates determined via the tracer-injection method)

$\theta_{\dot{m}_{C(s),produced},12} = \frac{\rho_{C(s)} R_u T_{sample}}{P_{plume}} \dot{n}_{plume,gas}$
$\theta_{\dot{m}_{C(s),produced},13} = \frac{\rho_{C(s)} f_{v,measured} R_u}{P_{plume}} \dot{n}_{plume,gas}$
$\theta_{\dot{m}_{C(s),produced},14} = - \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{P_{plume}^2} \dot{n}_{plume,gas}$
$\theta_{\dot{m}_{C(s),produced},20} = \frac{\rho_{C(s)} f_{v,measured} R_u T_{sample}}{P_{plume}}$

Table A7: Sensitivity indices for destruction removal efficiency, DRE_i (used for calculation of systematic error in any species DRE determined via the tracer-injection method and for calculation of systematic error in any non-carbon-based species DRE determined via the carbon-balance method)

$\theta_{DRE_i,15} = -\frac{(X_{i,plume}-X_{i,\infty}) \dot{n}_{plume,gas} + X_{i,\infty} \frac{\dot{m}_{FG}}{M_{\infty}}}{X_{i,FG} \dot{m}_{FG}} \times 100$
$\theta_{DRE_i,16} = \frac{(X_{i,plume}-X_{i,\infty}) \dot{n}_{plume,gas}}{X_{i,FG} \frac{\dot{m}_{FG}^2}{M_{FG}}} \times 100$
$\theta_{DRE_i,20} = -\frac{(X_{i,plume}-X_{i,\infty})}{X_{i,FG} \frac{\dot{m}_{FG}}{M_{FG}}} \times 100$
$\theta_{DRE_i,21} = -\frac{\dot{n}_{plume,gas}}{X_{i,FG} \frac{\dot{m}_{FG}}{M_{FG}}} \times 100$
$\theta_{DRE_i,22} = \frac{\dot{n}_{plume,gas} \frac{\dot{m}_{FG}}{M_{\infty}}}{X_{i,FG} \frac{\dot{m}_{FG}}{M_{FG}}} \times 100$
$\theta_{DRE_i,23} = \frac{(X_{i,plume}-X_{i,\infty}) \dot{n}_{plume,gas} + X_{i,\infty} \frac{\dot{m}_{FG}}{M_{\infty}}}{X_{i,FG} \frac{\dot{m}_{FG}}{M_{FG}}} \times 100$

The systematic error on a gaseous species emission rate defined by Eq. (3.13) in the manuscript can now be evaluated with Eq. (A.10) using the sensitivity index expressions from Table A5 and appropriate component systematic error values (such as those specified in Table A1):

$$B_{\dot{m}_{i,produced}} = \left(\left[\theta_{\dot{m}_{i,produced},16} B_{x_{16}} \right]^2 + \sum_{i=20}^{23} \left[\theta_{\dot{m}_{i,produced},i} B_{x_i} \right]^2 \right)^{1/2} \quad (A.10)$$

Similarly, the systematic error on the black carbon emission rate defined by Eq. (3.21) in the manuscript can be evaluated with Eq. (A.11) using the sensitivity index expressions from Table A6 and appropriate component systematic error values (such as those specified in Table A1):

$$B_{\dot{m}_{C(s),produced}} = \left(\sum_{i=12}^{14} \left[\theta_{\dot{m}_{C(s),produced},i} B_{x_i} \right]^2 + \left[\theta_{\dot{m}_{i,produced},20} B_{x_{20}} \right]^2 \right)^{1/2} \quad (A.11)$$

Finally, the systematic error on the destruction removal efficiency defined by Eq. (A.9) can be evaluated with Eq. (A.12) using the sensitivity index expressions from Table A7 and appropriate component systematic error values (such as those specified in Table A1):

$$B_{DRE_i} = \left(\sum_{i=15}^{16} [\theta_{DRE_i,i} B_{x_i}]^2 + \sum_{i=20}^{23} [\theta_{m_{i,produced},i} B_{x_i}]^2 \right)^{1/2} \quad (\text{A.12})$$

The systematic error can then be combined in quadrature with the experimental precision error (Eq. (A.2)) to determine the total uncertainty on a set of measurements in accordance with Eq. (A.3).

A4.2 Sensitivity Indices for Soot and Carbon-Based Gas-Phase Emission Rates using Carbon-Balance to Calculate $\dot{n}_{plume,gas}$

As mentioned in Section A4, for calculation of carbon-based species emission rates or carbon-based species DRE using the carbon-balance method there is a lack of independence between the calculated plume flow rate and the equations used to evaluate the species emission rate or DRE. For emission rates of gas-phase carbon-based species calculated with Eq. (3.13) of the manuscript, the applicable sensitivity indices are given in Table A8. For black carbon emission rates calculated with Eq. (3.21) of the manuscript, the relevant sensitivity indices are given in Table A9. For carbon-based species DRE calculated with Eq. (A.9), the relevant sensitivity indices are given in Table A10.

Table A8: Sensitivity indices for carbon-based gas emission rates calculated with the carbon-balance method

$\theta_{\dot{m}_{i,produced},1} = M_i(X_{i,plume} - X_{i,\infty})\theta_{\dot{n}_{plume,gas},1}$
$\theta_{\dot{m}_{i,produced},2} = M_i(X_{i,plume} - X_{i,\infty})\theta_{\dot{n}_{plume,gas},2}$
$\theta_{\dot{m}_{i,produced},3} = M_i(X_{i,plume} - X_{i,\infty})\theta_{\dot{n}_{plume,gas},3}$
$\theta_{\dot{m}_{i,produced},4} = \theta_{\dot{m}_{i,produced},6} = \theta_{\dot{m}_{i,produced},8} = \frac{\theta_{\dot{m}_{i,produced},10}}{\#C_{CmHn}} = M_i(X_{i,plume} - X_{i,\infty})\theta_{\dot{n}_{plume,gas},i}$
$\theta_{\dot{m}_{i,produced},5} = \theta_{\dot{m}_{i,produced},7} = \theta_{\dot{m}_{i,produced},9} = \frac{\theta_{\dot{m}_{i,produced},11}}{\#C_{CmHn}} = M_i(X_{i,plume} - X_{i,\infty})\theta_{\dot{n}_{plume,gas},i}$
$\theta_{\dot{m}_{i,produced},12} = M_i(X_{i,plume} - X_{i,\infty})\theta_{\dot{n}_{plume,gas},12}$
$\theta_{\dot{m}_{i,produced},13} = M_i(X_{i,plume} - X_{i,\infty})\theta_{\dot{n}_{plume,gas},13}$
$\theta_{\dot{m}_{i,produced},14} = M_i(X_{i,plume} - X_{i,\infty})\theta_{\dot{n}_{plume,gas},14}$
$\theta_{\dot{m}_{i,produced},15} = M_i \left((X_{i,plume} - X_{i,\infty})\theta_{\dot{n}_{plume,gas},15} + \left\{ X_{i,FG} \frac{\dot{m}_{FG}}{M_{FG}^2} \right\}_{inert} \right)$
$\theta_{\dot{m}_{i,produced},16} = M_i \left((X_{i,plume} - X_{i,\infty})\theta_{\dot{n}_{plume,gas},16} - \left\{ X_{i,FG} \frac{1}{M_{FG}} \right\}_{inert} + X_{i,\infty} \frac{1}{M_{\infty}} \right)$
$\theta_{\dot{m}_{i,produced},21} = M_i \left(\dot{n}_{plume,gas} + (X_{i,plume} - X_{i,\infty})\theta_{\dot{n}_{plume,gas},i} \right)$
$\theta_{\dot{m}_{i,produced},22} = M_i \left(-\dot{n}_{plume,gas} + (X_{i,plume} - X_{i,\infty})\theta_{\dot{n}_{plume,gas},i} + \frac{\dot{m}_{FG}}{M_{\infty}} \right)$
$\theta_{\dot{m}_{i,produced},23} = M_i \left((X_{i,plume} - X_{i,\infty})\theta_{\dot{n}_{plume,gas},3} - \frac{\dot{m}_{FG}}{M_{FG}} \right)$

Table A9: Sensitivity indices for black carbon emission rates calculated with the carbon-balance method

$\theta_{\dot{m}_{C(s)},produced,1} = \rho_{C(s)}f_{v,measured} \frac{R_u T_{sample}}{P_{plume}} \theta_{\dot{n}_{plume,gas},1}$
$\theta_{\dot{m}_{C(s)},produced,2} = \rho_{C(s)}f_{v,measured} \frac{R_u T_{sample}}{P_{plume}} \theta_{\dot{n}_{plume,gas},2}$
$\theta_{\dot{m}_{C(s)},produced,3} = \rho_{C(s)}f_{v,measured} \frac{R_u T_{sample}}{P_{plume}} \theta_{\dot{n}_{plume,gas},3}$
$\theta_{\dot{m}_{C(s)},produced,4} = \theta_{\dot{m}_{C(s)},produced,6} = \theta_{\dot{m}_{C(s)},produced,8} = \frac{\theta_{\dot{m}_{C(s)},produced,10}}{\#C_{CmHn}} = \rho_{C(s)}f_{v,measured} \frac{R_u T_{sample}}{P_{plume}} \theta_{\dot{n}_{plume,gas},i}$
$\theta_{\dot{m}_{C(s)},produced,5} = \theta_{\dot{m}_{C(s)},produced,7} = \theta_{\dot{m}_{C(s)},produced,9} = \frac{\theta_{\dot{m}_{C(s)},produced,11}}{\#C_{CmHn}} = \rho_{C(s)}f_{v,measured} \frac{R_u T_{sample}}{P_{plume}} \theta_{\dot{n}_{plume,gas},i}$
$\theta_{\dot{m}_{C(s)},produced,12} = \frac{\rho_{C(s)}R_u T_{sample}}{P_{plume}} \left(\dot{n}_{plume,gas} + f_{v,measured} \theta_{\dot{n}_{plume,gas},12} \right)$
$\theta_{\dot{m}_{C(s)},produced,13} = \frac{\rho_{C(s)}f_{v,measured}R_u}{P_{plume}} \left(\dot{n}_{plume,gas} + T_{sample} \theta_{\dot{n}_{plume,gas},13} \right)$
$\theta_{\dot{m}_{C(s)},produced,14} = \frac{\rho_{C(s)}f_{v,measured}R_u T_{sample}}{P_{plume}} \left(\theta_{\dot{n}_{plume,gas},14} - \frac{\dot{n}_{plume,gas}}{P_{plume}} \right)$
$\theta_{\dot{m}_{C(s)},produced,15} = \rho_{C(s)}f_{v,measured} \frac{R_u T_{sample}}{P_{plume}} \theta_{\dot{n}_{plume,gas},15}$
$\theta_{\dot{m}_{C(s)},produced,16} = \rho_{C(s)}f_{v,measured} \frac{R_u T_{sample}}{P_{plume}} \theta_{\dot{n}_{plume,gas},16}$

Table A10: Sensitivity indices for DRE of a carbon-based species calculated with the carbon-balance method

$\theta_{DRE_{i,1}} = -\frac{(X_{i,plume}-X_{i,\infty})}{X_{i,FG}\frac{\dot{m}_{FG}}{M_{FG}}} \theta_{\dot{n}_{plume,gas,1}} \times 100$
$\theta_{DRE_{i,2}} = -\frac{(X_{i,plume}-X_{i,\infty})}{X_{i,FG}\frac{\dot{m}_{FG}}{M_{FG}}} \theta_{\dot{n}_{plume,gas,2}} \times 100$
$\theta_{DRE_{i,3}} = -\frac{(X_{i,plume}-X_{i,\infty})}{X_{i,FG}\frac{\dot{m}_{FG}}{M_{FG}}} \theta_{\dot{n}_{plume,gas,3}} \times 100$
$\theta_{DRE_{i,4}} = \theta_{DRE_{i,6}} = \theta_{DRE_{i,8}} = \frac{\theta_{DRE_{i,10}}}{\#C,CmHn} = -\frac{(X_{i,plume}-X_{i,\infty})}{X_{i,FG}\frac{\dot{m}_{FG}}{M_{FG}}} \theta_{\dot{n}_{plume,gas,i}} \times 100$
$\theta_{DRE_{i,5}} = \theta_{DRE_{i,7}} = \theta_{DRE_{i,9}} = \frac{\theta_{DRE_{i,11}}}{\#C,CmHn} = -\frac{(X_{i,plume}-X_{i,\infty})}{X_{i,FG}\frac{\dot{m}_{FG}}{M_{FG}}} \theta_{\dot{n}_{plume,gas,i}} \times 100$
$\theta_{DRE_{i,12}} = -\frac{(X_{i,plume}-X_{i,\infty})}{X_{i,FG}\frac{\dot{m}_{FG}}{M_{FG}}} \theta_{\dot{n}_{plume,gas,12}} \times 100$
$\theta_{DRE_{i,13}} = -\frac{(X_{i,plume}-X_{i,\infty})}{X_{i,FG}\frac{\dot{m}_{FG}}{M_{FG}}} \theta_{\dot{n}_{plume,gas,13}} \times 100$
$\theta_{DRE_{i,14}} = -\frac{(X_{i,plume}-X_{i,\infty})}{X_{i,FG}\frac{\dot{m}_{FG}}{M_{FG}}} \theta_{\dot{n}_{plume,gas,14}} \times 100$
$\theta_{DRE_{i,15}} = -\left(\frac{(X_{i,plume}-X_{i,\infty})(\dot{n}_{plume,gas} + M_{FG}\theta_{\dot{n}_{plume,gas,15}}) + X_{i,\infty}\frac{\dot{m}_{FG}}{M_{\infty}}}{X_{i,FG}\dot{m}_{FG}}\right) \times 100$
$\theta_{DRE_{i,16}} = 0$
$\theta_{DRE_{i,21}} = -\frac{\dot{n}_{plume,gas} + (X_{i,plume}-X_{i,\infty})\theta_{\dot{n}_{plume,gas,i}}}{X_{i,FG}\frac{\dot{m}_{FG}}{M_{FG}}} \times 100$
$\theta_{DRE_{i,22}} = \frac{\dot{n}_{plume,gas} - \frac{\dot{m}_{FG}}{M_{\infty}}(X_{i,plume}-X_{i,\infty})\theta_{\dot{n}_{plume,gas,i}}}{X_{i,FG}\frac{\dot{m}_{FG}}{M_{FG}}} \times 100$
$\theta_{DRE_{i,23}} = \frac{(X_{i,plume}-X_{i,\infty})\dot{n}_{plume,gas} + X_{i,\infty}\frac{\dot{m}_{FG}}{M_{\infty}}}{X_{i,FG}\frac{2\dot{m}_{FG}}{M_{FG}}} \times 100$

The sensitivity indices Table A8, Table A9 and Table A10 are written in terms of $\theta_{\dot{n}_{plume,gas,i}}$ for consistency and simplicity of presentation. The dependence of $\dot{n}_{plume,gas}$ and the overall emission rate or DRE on the measured concentrations of the species being evaluated are accounted for with the sensitivity indices $\theta_{f,21}$ and $\theta_{f,22}$. For example, to determine the systematic error of a carbon-based gaseous species emission rate measured using the carbon-balance method (e.g. CH₄), Eq. (A.13) would be used with the sensitivity indices from Table A8:

$$B_{\dot{m}_{CH_4,produced}} = \left(\sum_{i=1}^7 [\theta_{\dot{m}_{CH_4,produced,i}} B_{x_i}]^2 + \sum_{i=10}^{16} [\theta_{\dot{m}_{CH_4,produced,i}} B_{x_i}]^2 + \sum_{i=21}^{22} [\theta_{\dot{m}_{CH_4,produced,i}} B_{x_i}]^2 \right)^{1/2} \quad (A.13)$$

Here the indices $\theta_{f,21}$ and $\theta_{f,22}$ are used in place of the specific indices for CH₄ ($\theta_{f,8}$ and $\theta_{f,9}$) when evaluating the systematic error in the CH₄ emission rate. Similarly,

if the species of interest were CO, $\theta_{f,21}$ and $\theta_{f,22}$ would be used in place of $\theta_{f,6}$ and $\theta_{f,7}$ (specific indices for CO). Finally, if the species of interest were CO₂, $\theta_{f,21}$ and $\theta_{f,22}$ would be used in place of $\theta_{f,4}$ and $\theta_{f,5}$ (specific indices for CO₂) and, if CO₂ were present as a diluent in the fuel stream, $\theta_{f,23}$ would be used in place of $\theta_{f,3}$.

The calculation of a black carbon emission rate using the carbon-balance method to calculate the plume flow rate is more straightforward. In this case the sensitivity indices given in Table A9 should be evaluated as follows:

$$B_{\dot{m}_{C(s)},produced} = \left(\sum_{i=1}^{16} [\theta_{\dot{m}_{C(s)},produced,i} B_{x_i}]^2 \right)^{1/2} \quad (\text{A.14})$$

Similar to the procedure used to evaluate Eq. (A.13), calculation of a DRE using the carbon-balance method to calculate the plume flow rate utilizes indices $\theta_{f,21}$ through $\theta_{f,23}$. In this case the sensitivity indices given in Table A10 should be evaluated as follows (e.g. CH₄):

$$B_{DRE_{CH_4}} = \left(\sum_{i=1}^7 [\theta_{DRE_{CH_4},i} B_{x_i}]^2 + \sum_{i=10}^{16} [\theta_{DRE_{CH_4},i} B_{x_i}]^2 + \sum_{i=21}^{23} [\theta_{DRE_{CH_4},i} B_{x_i}]^2 \right)^{1/2} \quad (\text{A.15})$$

This systematic error for either the gas-phase (Eq. (A.13)) or black carbon (Eq. (A.14)) emission rate or the DRE (Eq. (A.15)) can then be combined in quadrature with the experimental precision error (Eq. (A.2)) to determine the total uncertainty on a set of measurements in accordance with Eq. (A.3).

A5 Synthetic Data and Experimental Measurement Systematic Error Comparison

A comparison with the systematic error of experimental measurements can be used to validate the expected systematic errors calculated for the synthetic data. The systematic

error on the measured combustion efficiency (expressed as an absolute error, i.e. 2% error on 95% efficiency is equivalent to error range of 93-97%) calculated with the carbon-balance method falls at the low end of the range expected as shown in Figure A1. The systematic error on the measured combustion efficiency calculated with the tracer-injection method falls just above the range expected for the synthetic data. This results from a higher component error on the tracer gas species for the current experimental measurements than that used for the synthetic data, where it was assumed that a specifically tailored instrument for measuring the tracer (e.g. a cavity ringdown gas analyzer) could be used to improve accuracy.

Figure A2 shows the systematic errors of species yield of both carbon monoxide and nitrogen oxides measured using the carbon-balance method. Here the errors are plotted relative to the measured value (i.e. as a percentage of the measured value). The respective systematic errors of the species yields were nearly identical using the carbon-balance and tracer-injection methods, where only the former are plotted in Figure A2 for clarity. Carbon monoxide and nitrogen oxides have slightly different detection limits when measured with the current gas analysis instrument which is reflected in the differences in the resulting systematic errors. The relative systematic error of a given species yield fits well with expected values from the synthetic data.

Figure A1: Comparison of absolute uncertainty of combustion efficiency for synthetic data and experimental measurements.

Figure A2: Comparison of relative uncertainty of species yields for synthetic data and experimental measurements.

Appendix B CO and Hydrocarbon Results, Analysis and Discussion

Carbon monoxide (CO) and hydrocarbon emissions from combustion processes are an important consideration as the primary gas-phase carbon-based emissions. CO yield, as shown in Figure B1, tends to decrease to as mass flow rate increases before levelling off at yield values unique to the different flare gases. For the HVY 4-Mix flare gas, which was tested on multiple burner sizes, there does not appear to be any discernable change among the different diameters tested. However, more apparent than any trend with flow rate or diameter are the differences in emission rates for the different flare gas compositions. As with the soot yield discussed previously, CO yields increased from the methane-based flare gases, which yielded the least CO, to ethylene which yielded the highest CO. The CO yields for propane and ethylene were approximately 2 and 3 times greater than the CO yield for the HVY 4-Mix respectively.

Figure B1: CO yield calculated using the carbon balance method for the 38.1, 50.8 and 76.2 mm burners with AVG 6-Mix, HVY 4-Mix, ethylene, methane, and propane flare gas mixtures.

Methane yields for the flames tested are shown in Figure B2a. For both the propane and ethylene flare gases, the methane emissions are essentially zero. For the methane-based flare gases there are minimal methane emissions at the lower flow rates on all burners, however the uncertainties are high and include the possibility of zero emissions. At higher flow rates the emissions approach zero and the uncertainties decrease. Ethane yields for the flames tested are shown in Figure B2b and are essentially zero for all cases. Propane yields for the flames tested are shown in Figure B2c. For the methane-based flare gases on all burners the propane yield is zero or near zero with the uncertainties including the possibility of zero yield. For the test flow rates using ethylene flare gas, negligible propane emissions were detected. Propane yields from the propane burning flames were in the range of 0.5 g/kg-flare-gas. Ethylene yields for the flames tested are shown in Figure B2d. The yields of ethylene from propane burning flames

were negligible, whereas for two of the four ethylene cases, the yield of ethylene is in the range of 1 g/kg-flare-gas.

The results presented suggest that hydrocarbon emissions from turbulent non-premixed diffusion flames are near zero for flames burning in quiescent conditions with high-heating values. A tentative further conclusion is that the form of the hydrocarbons emitted from a flare are likely to be unburned hydrocarbons of the same chemical structure as the flare gas and not reformed hydrocarbons.

Figure B2: a) CH₄, b) C₂H₆, c) C₃H₈, d) C₂H₄ yields calculated using the carbon balance method for the 38.1, 50.8 and 76.2 mm burners with AVG 6-Mix, HVY 4-Mix, ethylene, methane and propane flare gas mixtures.

Appendix C Flame Length Results, Analysis and Discussion

Flame length was measured using the equipment and methodology outlined in Section 2.6. As shown in Figure C1, the measured flame lengths for all flare gases and all burner sizes tested increased with minimal scatter as the mass flow rate was increased. In Figure C2, the measured flame lengths are compared to flame lengths calculated using the correlation defined by Delichatsios (1993) (Eq. (C.1) below) for flames with Fire Froude numbers (See Eq. (1.3)) less than 5. The available data for all tests fits very well with the flame length correlation.

$$L_f = 13.5d_e \frac{Fr_f^{0.4}}{f_s(1 + 0.07Fr_f^2)^{0.2}} \left(\frac{\rho_e}{\rho_\infty}\right)^{0.5} \quad (C.1)$$

Figure C1: Measured flame length for 38.1, 50.8 and 76.2 mm burners with HVY 4-Mix, ethylene and propane flare gas mixtures.

Figure C2: Comparison of measured flame length and flame length calculated using Delichatsios (1993) correlation for 38.1, 50.8 and 76.2 mm burners with HVY 4-Mix, ethylene and propane flare gas mixtures.

Appendix D Soot Yield Tabulated Results

Flare Gas Mixture	Diameter (mm)	Set Flow (SLPM)	Total Flow (kg/s)	Reynolds number	Global Froude number	Soot Yield (kg/kg)	Soot Yield Uncertainty (kg/kg)
HVY 4-Mix	38.1	34.20	5.46E-04	1925	1.03E-02	1.34E-03	2.80E-04
		61.56	9.82E-04	3466	1.85E-02	1.29E-03	2.69E-04
		102.61	1.64E-03	5777	3.06E-02	1.23E-03	2.56E-04
		150.49	2.40E-03	8474	4.48E-02	8.78E-04	1.83E-04
		218.90	3.49E-03	12325	6.43E-02	3.84E-04	7.97E-05
	50.8	30.40	4.85E-04	1283	4.41E-03	1.25E-03	2.61E-04
		60.80	9.70E-04	2567	8.80E-03	1.29E-03	2.68E-04
		109.45	1.75E-03	4623	1.58E-02	1.14E-03	2.37E-04
		182.41	2.91E-03	7705	2.64E-02	1.05E-03	2.17E-04
		224.98	3.59E-03	9501	3.24E-02	1.02E-03	2.11E-04
	76.2	27.36	4.37E-04	770	1.49E-03	1.09E-03	2.28E-04
		68.41	1.09E-03	1926	3.68E-03	1.02E-03	2.11E-04
		136.81	2.18E-03	3852	7.38E-03	1.07E-03	2.23E-04
		218.90	3.49E-03	6163	1.17E-02	1.10E-03	2.29E-04
		246.26	3.93E-03	6935	1.34E-02	8.90E-04	1.85E-04
Ethylene	50.8	30.40	6.30E-04	1668	6.53E-03	1.59E-02	3.42E-03
		60.80	1.27E-03	3370	1.32E-02	1.24E-02	2.57E-03
		109.45	2.27E-03	6004	2.36E-02	1.07E-02	2.20E-03
		182.41	3.77E-03	9976	3.91E-02	8.97E-03	1.84E-03
Propane	50.8	182.41	4.17E-04	1398	2.25E-03	7.74E-03	1.76E-03
		30.40	1.01E-03	3366	5.38E-03	6.20E-03	1.30E-03
		60.80	2.00E-03	6686	1.07E-02	5.25E-03	1.08E-03
		109.45	3.55E-03	11896	1.88E-02	4.70E-03	9.64E-04

Flare Gas Mixture	Diameter (mm)	Set Flow (SLPM)	Total Flow (kg/s)	Reynolds number	Global Froude number	Soot Yield (kg/kg)	Soot Yield Uncertainty (kg/kg)
Methane	50.8	60.80	7.25E-04	1770	1.18E-02	8.54E-05	1.81E-05
		109.45	1.31E-03	3187	2.12E-02	8.11E-05	1.71E-05
		182.41	2.18E-03	5311	3.53E-02	7.35E-05	1.55E-05
	76.2	68.41	8.16E-04	1328	4.93E-03	6.84E-05	1.45E-05
		136.81	1.63E-03	2656	9.89E-03	5.95E-05	1.25E-05
		246.26	2.94E-03	4780	1.80E-02	7.26E-05	1.53E-05
AVG 6-Mix	50.8	30.40	4.34E-04	1080	5.48E-03	5.35E-04	8.05E-05
		60.80	8.68E-04	2160	1.09E-02	4.90E-04	1.03E-04
		109.45	1.56E-03	3882	1.95E-02	5.69E-04	1.19E-04
		182.41	2.60E-03	6480	3.26E-02	4.13E-04	8.62E-05
		267.54	3.82E-03	9505	4.73E-02	3.56E-04	7.42E-05
	76.2	27.36	3.91E-04	648	1.80E-03	3.93E-04	8.30E-05
		68.41	9.76E-04	1620	4.50E-03	4.32E-04	9.05E-05
		136.81	1.95E-03	3240	9.04E-03	4.52E-04	9.43E-05
		246.26	3.51E-03	5833	1.65E-02	4.27E-04	8.89E-05
		410.43	5.86E-03	9722	2.73E-02	3.70E-04	7.78E-05

Appendix E NO_x Yield Tabulated Results

Flare Gas Mixture	Diameter (mm)	Set Flow (SLPM)	Total Flow (kg/s)	NO _x Yield (kg/kg)	NO _x Yield Uncertainty (kg/kg)	NO _x Yield (kg/GJ)	NO _x Yield Uncertainty (kg/GJ)
HVY 4-Mix	38.1	34.20	5.46E-04	1.98E-03	1.19E-03	0.037	0.022
		61.56	9.82E-04	2.08E-03	9.77E-04	0.039	0.018
		102.61	1.64E-03	2.09E-03	7.69E-04	0.039	0.014
		150.49	2.40E-03	2.13E-03	4.93E-04	0.040	0.009
		218.90	3.49E-03	2.13E-03	3.15E-04	0.040	0.006
	50.8	30.40	4.85E-04	1.94E-03	1.94E-03	0.036	0.036
		60.80	9.70E-04	1.95E-03	1.23E-03	0.036	0.023
		109.45	1.75E-03	1.97E-03	7.98E-04	0.037	0.015
		182.41	2.91E-03	2.01E-03	4.37E-04	0.038	0.008
		224.98	3.59E-03	2.00E-03	3.00E-04	0.037	0.006
	76.2	27.36	4.37E-04	1.81E-03	2.45E-03	0.034	0.046
		68.41	1.09E-03	1.91E-03	1.05E-03	0.036	0.020
		136.81	2.18E-03	2.02E-03	6.22E-04	0.038	0.012
		218.90	3.49E-03	2.03E-03	3.16E-04	0.038	0.006
		246.26	3.93E-03	2.03E-03	3.89E-04	0.038	0.007
Ethylene	50.8	30.40	6.30E-04	2.31E-03	1.00E-03	0.046	0.020
		60.80	1.27E-03	2.09E-03	1.03E-03	0.042	0.020
		109.45	2.27E-03	2.03E-03	5.26E-04	0.040	0.010
		182.41	3.77E-03	2.06E-03	2.88E-04	0.041	0.006
Propane	50.8	182.41	4.17E-04	1.78E-03	1.42E-03	0.035	0.028
		30.40	1.01E-03	1.69E-03	9.29E-04	0.034	0.018
		60.80	2.00E-03	1.78E-03	5.99E-04	0.035	0.012
		109.45	3.55E-03	1.79E-03	3.01E-04	0.035	0.006

Flare Gas Mixture	Diameter (mm)	Set Flow (SLPM)	Total Flow (kg/s)	NO _x Yield (kg/kg)	NO _x Yield Uncertainty (kg/kg)	NO _x Yield (kg/GJ)	NO _x Yield Uncertainty (kg/GJ)
Methane	50.8	60.80	7.25E-04	2.34E-03	2.50E-03	0.042	0.045
		109.45	1.31E-03	2.33E-03	1.33E-03	0.042	0.024
		182.41	2.18E-03	2.10E-03	7.08E-04	0.038	0.013
	76.2	68.41	8.16E-04	2.16E-03	2.31E-03	0.039	0.042
		136.81	1.63E-03	2.23E-03	9.95E-04	0.040	0.018
		246.26	2.94E-03	2.22E-03	5.22E-04	0.040	0.009
AVG 6-Mix	50.8	30.40	4.34E-04	1.36E-03	2.90E-03	0.027	0.057
		60.80	8.68E-04	1.88E-03	2.19E-03	0.037	0.043
		109.45	1.56E-03	1.78E-03	1.14E-03	0.035	0.022
		182.41	2.60E-03	1.86E-03	6.25E-04	0.037	0.012
		267.54	3.82E-03	2.02E-03	3.93E-04	0.040	0.008
	76.2	27.36	3.91E-04	1.57E-03	3.69E-03	0.031	0.072
		68.41	9.76E-04	1.62E-03	1.90E-03	0.032	0.037
		136.81	1.95E-03	1.96E-03	8.86E-04	0.038	0.017
		246.26	3.51E-03	2.01E-03	4.55E-04	0.039	0.009
		410.43	5.86E-03	2.03E-03	2.68E-04	0.040	0.005

Appendix F Combustion Efficiency Tabulated Results

Flare Gas Mixture	Diameter (mm)	Set Flow (SLPM)	Total Flow (kg/s)	Mixed-Phase Efficiency (%)	Mixed-Phase Uncertainty (%)	Gas-Phase Efficiency (%)	Gas-Phase Uncertainty (%)
HVY 4-Mix	38.1	34.20	5.46E-04	99.73	0.10	99.90	0.09
		61.56	9.82E-04	99.70	0.08	99.86	0.08
		102.61	1.64E-03	99.76	0.07	99.92	0.06
		150.49	2.40E-03	99.80	0.05	99.92	0.04
		218.90	3.49E-03	99.91	0.03	99.96	0.02
	50.8	30.40	4.85E-04	99.60	0.14	99.76	0.13
		60.80	9.70E-04	99.71	0.09	99.88	0.09
		109.45	1.75E-03	99.78	0.06	99.93	0.06
		182.41	2.91E-03	99.80	0.04	99.94	0.03
		224.98	3.59E-03	99.82	0.04	99.95	0.02
	76.2	27.36	4.37E-04	99.65	0.17	99.79	0.16
		68.41	1.09E-03	99.75	0.08	99.88	0.07
		136.81	2.18E-03	99.78	0.05	99.91	0.04
		218.90	3.49E-03	99.81	0.04	99.95	0.02
		246.26	3.93E-03	99.87	0.03	99.99	0.02
Ethylene	50.8	30.40	6.30E-04	97.84	0.38	99.69	0.07
		60.80	1.27E-03	98.27	0.30	99.71	0.07
		109.45	2.27E-03	98.63	0.26	99.87	0.04
		182.41	3.77E-03	98.80	0.21	99.84	0.02
Propane	50.8	182.41	4.17E-04	98.84	0.23	99.78	0.12
		30.40	1.01E-03	99.07	0.17	99.83	0.07
		60.80	2.00E-03	99.24	0.14	99.88	0.04
		109.45	3.55E-03	99.30	0.12	99.88	0.02

Flare Gas Mixture	Diameter (mm)	Set Flow (SLPM)	Total Flow (kg/s)	Mixed-Phase Efficiency (%)	Mixed-Phase Uncertainty (%)	Gas-Phase Efficiency (%)	Gas-Phase Uncertainty (%)
Methane	50.8	60.80	7.25E-04	99.88	0.15	99.89	0.15
		109.45	1.31E-03	99.92	0.08	99.93	0.08
		182.41	2.18E-03	99.95	0.04	99.96	0.04
	76.2	68.41	8.16E-04	99.84	0.14	99.85	0.14
		136.81	1.63E-03	99.93	0.06	99.94	0.06
		246.26	2.94E-03	99.95	0.03	99.96	0.03
AVG 6-Mix	50.8	30.40	4.34E-04	99.50	0.26	99.57	0.26
		60.80	8.68E-04	99.78	0.14	99.85	0.14
		109.45	1.56E-03	99.83	0.07	99.91	0.07
		182.41	2.60E-03	99.86	0.04	99.92	0.04
		267.54	3.82E-03	99.89	0.03	99.94	0.02
	76.2	27.36	3.91E-04	98.73	0.24	98.79	0.24
		68.41	9.76E-04	99.81	0.12	99.87	0.12
		136.81	1.95E-03	99.89	0.06	99.95	0.06
		246.26	3.51E-03	99.88	0.03	99.94	0.03
		410.43	5.86E-03	99.91	0.02	99.96	0.02