https://dx.doi.org/10.4314/ijs.v22i2.13

SELF-CONSISTENT ESTIMATES OF EMISSION FACTORS OF CARBON-CONTAINING POLLUTANTS FROM A TYPICAL GAS FLARE

Fawole, O. G.[1, 2*], Cai, X. -M.[2], Nikolova, I.[2], MacKenzie, A. R.[2, 3]
[1]Environmental Pollution Research Laboratory (EPRL), Department of Physics and Engineering Physics, Obafemi Awolowo University, Ile-Ife, Nigeria 220005
[2]School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK
[3]Birmingham Institute of Forest Research, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK
*Corresponding author: gofawole@oauife.edu.ng

(Received: 5th November, 2019; Accepted: 5th June, 2020)

ABSTRACT

This study proposes an approach for estimating the emission of soot, carbon monoxide (CO) and carbon-dioxide (CO_2) from a typical gas flare. The estimations depend on the quantity and varying composition of the natural gas, flame dynamics (represented by the fire Froude number, Fr_f) and the equivalence ratio, ϕ, of the fuel-air mixture. Soot emission estimates are presented as a function of fire Froude number for gases used in lab-based test in order to validate the scheme and for two real-world fuel gas compositions. The mass-weighted carbon-hydrogen ratio (C:H) of the fuel gas compositions are 0.25 and 0.29 which are two extreme cases in terms of density. The soot yield of the lab-based test case was scaled up to estimate the soot yield of a full scale flare using the Richardson number as the scaling parameter. When all other variables are held constant at values characteristics of real-world flares, a difference of 16 % in the fuel-gas density, as indicated by the carbon-hydrogen ratio, results in an increase of the emission factors (EF) of soot, CO and CO_2 by factors of ~3, ~1.4 and ~1.7, measured in g/m^3, respectively. For both fuel gas compositions, the ratio of EF_{soot} to EF_{CO} at the fuel-lean region $\phi < 1$) is higher. The ratio lies in the range 0.031 – 0.13 and 0.0012 – 0.0055 for the fuel-lean ($\phi < 1$) and fuel-rich ($\phi > 1$) regions, respectively. The approach proposed and results obtained may be adopted to generate emissions inventories of emission species associated with gas flaring on regional and global scales.

Keywords: gas flaring; soot; natural gas; emission factor; black carbon; equivalence ratio

INTRODUCTION

Natural gas comprises mainly of hydrocarbons occurring in geological deposits, and consists mainly of methane. It includes both "non-associated" gas, originating from fields producing hydrocarbons only in gaseous form, and "associated" gas, produced in association with crude oil and separated at a flow station (IEA, 2012). Gas flaring and booming are the widely used methods of disposing of some of these gases, which are often termed unwanted or hazardous. Gas flaring is the controlled burning, in open flame, of associated gas that is produced at various stages of crude oil exploration and exploitation (Beychok, 1994; EEA, 2006). For the purpose of this study, the flared gas will be referred to as fuel gas. In recent years, especially 2014 - 2016, there had been renewed efforts at the estimation of emissions from gas flaring activities as well as quantifying the contributions of gas flaring to atmospheric pollution, particularly in the Bakken region of North Dakota, USA and the Arctic (Li *et al.*, 2016; Schwarz *et al.*, 2015; Weyant *et al.*, 2016).

While carbon dioxide (CO_2) is an inevitable consequence of flaring, a number of undesired pollutants are emitted during gas flaring process. The undesirable pollutants are emitted when the combustion process is inefficient or incomplete as a result of incomplete oxidation of hydrocarbon species in the fuel gas or the ineffectiveness of the process (Flagan and Seinfeld, 2012; Fortner *et al.*, 2012). Globally, about 140 billion cubic meters (bcm) of gas was flared in 2011, an increase of 1.9 % from the preceding year (GGFR, 2012). This represents an estimated contribution of 350 million tons of CO_2 to global greenhouse gas (GHG) emissions. Noise, smoke (soot), heat radiation, nitrogen oxides ($NO_X = NO+NO_2$), carbon monoxide (CO), sulfur dioxide (SO_2) and Polycyclic Aromatic Hydrocarbons (PAH) are some of the environmental contaminants released during gas flaring process (Abdulkareem *et al.*, 2012; Almanza *et al.*, 2012; Johnson and Kostiuk, 2000; Kostiuk *et al.*, 2004; McDaniel and Tichenor, 1983; Obanijesu *et al.*, 2009; Sonibare *et al.*, 2010; Stone *et al.*, 1992).

The nature and quantity of pollutants given off during the combustion process depend on a number of factors which include air-fuel mass (or mole) ratio, fuel gas composition, fuel flow rate, mixing of fuel gas and air, efficiency of the burner and prevailing ambient meteorology (Castineira and Edgar, 2006; Fortner *et al.*, 2012; Ismail and Umukoro, 2016; Sivathanu and Faeth, 1990; Sonibare and Akeredolu, 2004; Talebi *et al.*, 2014; Torres *et al.*, 2012a; Torres *et al.*, 2012b). Studies have identified gas flaring as a prominent contributor to regional air pollution index especially in oil-producing regions of the world (Edwards *et al.*, 2014; Fawole *et al.*, 2016; Fawole *et al.*, 2017; Gilman *et al.*, 2013; Liousse *et al.*, 2019). About 1 – 8 % of global, 15 – 30 % of oil-rich regions and more than 50 % of Arctic black carbon (BC) emission could be attributed to gas flaring (Huang *et al.*, 2015; Stohl *et al.*, 2013).

Estimates of emission factors (EF) from gas flaring have been made using pilot-scale studies (McDaniel and Tichenor, 1983; Talebi *et al.*, 2014), lab-based studies (McEwen and Johnson, 2012), simulations (Almanza *et al.*, 2012; Ismail and Umukoro, 2016; Sonibare and Akeredolu, 2004) and field measurements (e.g., Sky-LOSA technique) (Johnson *et al.*, 2013; Johnson *et al.*, 2011).

Black carbon (BC), a principal light-absorbing species in the atmosphere has been identified as the second major contributor to global warming after CO_2 (Santos *et al.*, 2014). Fossil fuel-derived BC has equally been identified as a stronger global warming agent than biomass-derived BC (Bond *et al.*, 2013; Ramana *et al.*, 2010; Ramanathan and Carmichael, 2008). BC may also contribute significantly to visibility degradation (Feichter and Stier, 2012; Jacobson, 2002; Seinfeld, 2008; Tegen *et al.*, 1997). It also contribute a large fraction to the fine particulate mass (PM) fraction found in ambient air especially around highly populated and industrialized regions of the world (Chow *et al.*, 1996; Kirchstetter *et al.*, 1999).

Measuring soot (BC) yield in an open fire like gas flare is a difficult task (Johnson *et al.*, 2011). However, attempts have been made to quantify soot yield in terms of the fuel and fire characteristics, flow conditions and burner geometry in pilot-scale and lab-based studies (Becker and Liang, 1982; Delichatsios, 1993; Sivathanu and Faeth, 1990). Carbon conversion efficiency (CCE) is a measure of the extent of conversion of the carbon content of the fuel gas to carbon dioxide, usually expressed as a percentage (Bourguignon *et al.*, 1999). CCE is often used to determine the completeness of combustion and it can be as low as 62 % in associated gas flares (Strosher, 2000). At a CCE of about 99%, visible smoking can still be observed in a flare (Siegel, 1980). The carbon content of the fuel gas could be emitted as carbon dioxide, carbon monoxide, total hydrocarbon (THC) and BC. The amount of each fraction emitted depends on the degree of completeness of the combustion which could be estimated from the CCE.

This work aims to develop a simple self-consistent method which requires fewer inputs from the user and takes into account the flame dynamics to study the variation of CO, CO_2 and soot emission with varying fuel gas composition, flow characteristics, stack geometry and equivalence ratio in a typical gas flare. The characteristic physical and chemical parameters defining the flare are first introduced and are then used to derive a system of equations to estimate the EFs. The approach is validated by comparing the model outputs with results from similar test flares from literature. Finally, variation of EFs with realistic changes in fuel composition is examined and possible implication of results from the study on global emission inventories is discussed.

METHODOLOGY

Equivalence Ratio

For the purpose of this work, the degree of combustion is determined in terms of the amount of oxygen available for the combustion of the fuel gas which is measured as air to fuel mass ratio. The stoichiometric air-fuel ratio gives the theoretical proportion of air mass needed for the complete combustion of the fuel where A, F and s denote *'air'*, *'fuel'* and *'stoichiometric mixture'*, respectively. During combustion, stoichiometric mixture is not always and everywhere attained, hence, it is necessary to calculate the actual air to fuel ratio , where a denotes *'actual mixture'* (Flagan and Seinfeld, 2012). Equivalence ratio (ϕ) is defined as:

$$\phi = \frac{\left(\frac{A}{F}\right)_s}{\left(\frac{A}{F}\right)_a} \qquad (1)$$

Thus ϕ =1 is a stoichiometric, ϕ < 1 a fuel-lean (under-fired) and ϕ > 1 a fuel-rich (over-fired) mixture.

The quantity of combustion products, especially soot, varies significantly with the equivalence ratio, ϕ (Huang *et al.*, 2015). When ϕ <1 (excess air), combustion could be assumed to be complete with excess oxygen given off unreacted as a combustion by-product (Flagan and Seinfeld, 2012; McAllister *et al.*, 2011). The combustion products for an 'ideal' combustion (ϕ =1) are relatively easy to quantify as CO_2, water and fully oxidized products of any trace components (e.g., N_2 and H_2S converted to NO_2 and SO_2, respectively). Complete combustion is often not achieved in most flaring conditions as pyrolysis converts some of the fuel gas to many complex chemical species rather than the *'ideal'* CO_2, SO_2, NO_2 and H_2O (Leahey *et al.*, 2001; Strosher, 2000).

The products of combustion for ϕ >1 are more difficult to specify and estimate because there is not enough oxygen to completely burn off all of the fuel gas (Flagan and Seinfeld, 2012; McAllister *et al.*, 2011). Higher values of ϕ give rise to cooler flames that do not support fast combustion kinetics and, hence, favour the production of sooty flames (Stone *et al.*, 1992). Lower flame temperature reduces the buoyancy and mixing of fuel gas and air in the combustion zone (Stone *et al.*, 1992) with implications on how the emissions are dispersed into the ambient atmosphere.

Mole balancing equation

For an 'ideal' stoichiometric mixture (ϕ = 1) of a hydrocarbon (alkane) and air, the generalized equation for complete combustion is:

$$C_xH_y + \left(\frac{y}{4} + x\right) O_2 \rightarrow xCO_2 + \left(\frac{y}{2}\right) H_2O \qquad (2)$$

where *'x'* and *'y'* are integers, the relationship between which defines the hydrocarbon. For a mixture of various hydrocarbons, as in fuel gas, '*x*' and '*y*' are real numbers calculated from the molar composition of the gas. In a first step away from ideality, these calculated values of '*x*' and '*y*' can be scaled to take account of unburnt hydrocarbon. Taking into account the effects of the equivalence ratio (which is treated henceforth as an empirical input) and incomplete oxidation, as discussed above, a generalized combustion equation (GCE) is proposed as:

$$C_xH_y + \frac{1}{\phi}\left(\frac{y}{4} + x\right) O_2 \rightarrow pCO_2 + qCO + rC + vO_2 + \left(\frac{y}{2}\right) H_2O \qquad (3)$$

where *'p'*, *'q'*, *'r'* and *'v'* are real numbers whose values are determined by the degree of completeness of oxidation achieved in the flame. In forming equation (3), it is assumed that all hydrogen is converted to water. Hence, all black carbon is made up purely of elemental carbon and no PAH is emitted. The parameter '*v*' in equation (3), number of moles of 'unused' oxygen, is defined to ensure that all molar quantities are positive definite.

From equation (3), the following conservative relations can be obtained:

$$x = p + q + r \qquad (4a)$$

$$\frac{1}{\phi}\left(x + \frac{y}{4}\right) = p + \frac{q}{2} + v + \frac{y}{4} \qquad (4b)$$

From equations (4a) and (4b);

$$\begin{aligned} q &= \left(2x + \frac{y}{2}\right)\left(1 - \frac{1}{\phi}\right) + 2v - 2r \\ &= 2\left(x + \frac{y}{4}\right)\left(1 - \frac{1}{\phi}\right) + 2v - 2r \\ &= 2(OCOM)\left(1 - \frac{1}{\phi}\right) + 2v - 2r \qquad (4c) \end{aligned}$$

$$\begin{aligned} p &= NCAR - q - r \\ &= NCAR - \left(2(OCOM)\left(1 - \frac{1}{\phi}\right) + 2v - 2r\right) - r \qquad (4d) \end{aligned}$$

where *NCAR* $= x$ is the number of carbon atom in the hydrocarbon specie and *OCOM* the number of moles of oxygen requires by the hydrocarbon specie for stoichiometric mixture.

For ϕ > 1, it is assumed that ν = 0 (i.e. no unused oxygen)

Hence $q = \left(2x + \frac{y}{2}\right)\left(1 - \frac{1}{\phi}\right) - 2r$

For $\phi \le 1;\ v \ne 0$

Incomplete combustion of natural gas gives off CO and CO_2 in ratios which depend on the source and efficiency of the combustion process (Djuricin *et al.*, 2010). Formation of CO depends majorly on the amount of air available – lesser or in excess - for the combustion process (Bishop and Stedman, 1996). For gas flaring, the ratio of the emission factor of CO to that of CO_2 obtained from literature are 0.0024 (EEMS, 2008), 0.0032 (USEPA, 2014) and 0.0042 (UK Offshore Association see (Talebi *et al.*, 2014)). For this work, the USEPA value of 0.0032 will be used as it was obtained from a pilot study carried out on emissions from gas flares. From (USEPA, 2014),

$$\frac{EF_{co}}{EF_{co2}} = \frac{M_{co}q}{M_{co2}p} = 0.0032$$

where M_{co} and M_{co2} are the molar mass on CO and CO_2, respectively.

$$\frac{q}{p} = 0.005$$

$$\frac{q}{p} = \frac{2(OCOM)\left(1 - \frac{1}{\phi}\right) + 2v - 2r}{NCAR - 2(OCOM)\left(1 - \frac{1}{\phi}\right) - 2v + r} = 0.005 \qquad (5a)$$

Hence;

$$v = \frac{0.005NCAR - 2.01 * OCOM\left(1 - \frac{1}{\phi}\right) + 2.005r}{2.01} \qquad (5b)$$

$$\left.\begin{aligned} v &= \frac{0.005NCAR + 2.005r}{2.01} \\ q &= 2v - 2r \end{aligned}\right\} \phi = 1$$

Therefore, there are three equations (4a, 4b and 5b) relating four unknowns (*p, q, r, v*) and three input parameters (*x, y,* ϕ) which are insufficient to evaluate *p, q, r* and *v*. One further relationship is required.

In this study, a method is developed using the *fire Froude number*, Fr_f suggested by Delichatsios (1993) and improved upon by McEwen and Johnson (2012) as a basis to constrain parameter, *r*, for the 'unburned' carbon. In their experimental study, McEwen and Johnson (2012) plotted soot yields as a function of the fire Froude number (see Fig. 1). In this study, the soot yield from the lab-based experiment of McEwen and Johnson is scaled up to estimate the soot yield from a full-scale flare using a scaling parameter (Becker and Liang, 1982; Canteenwalla *et al.*, 2007). The scaled-up soot yield data is then used to constraint the term '*rC*' in the GCE (see equation 3) and '*r*' in eq. (5b) and, hence, obtain '*p*', and '*q*'.

Fire Froude number, Fr_f (eq. 6) is a dimensionless parameter related to the flame dynamics characteristics.

$$Fr_f = \frac{u_e f_s^{3/2}}{\left(\frac{\Delta T_f}{T_{amb}} g d_e\right)^{1/2} \left(\frac{\rho_e}{\rho_a}\right)^{1/4}} \qquad (6)$$

where $\frac{1}{s+1} = \frac{\phi}{\left(\frac{a}{f}\right)_s + \phi}$

s – air-fuel mass ratio, $\left(\frac{a}{f}\right)_a$

u_e – flue gas exit velocity (m/s)

T_{amb} – ambient temperature (K)

T_θ – adiabatic temperature (K), defined below

ΔT_f – flame temperature rise ($\Delta T_f = T_\theta - T_{amb}$) (K)

g – acceleration due to gravity (m/s^2)

d_e – stack diameter (m)

ρ_a, ρ_e – ambient and fuel gas density respectively (kg/m^3)

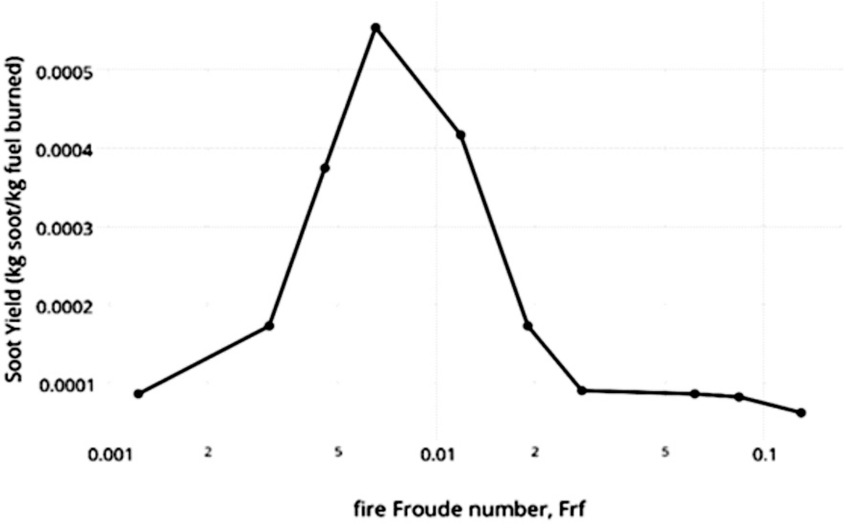

Figure 1: Soot yield as a function of fire Froude number (adapted from (McEwen and Johnson, 2012))

For this study, Fr_f of the combustion flame is dependent on the air-fuel mass ratio and hence on one of our variable, the equivalence ratio, ϕ. The adiabatic temperature, T_θ, for the different combustion type and fuel compositions is calculated as the roots of the quadratic in eq. (7).

$$h_i(T_\theta) - h_i(T_{amb}) = a_i(T_\theta - T_{amb}) + \frac{b_i}{2}(T_\theta{}^2 - T_{amb}{}^2) \qquad (7)$$

where h_i is the temperature-dependent molar specific enthalpy for the *i*th species of hydrocarbon; T_θ and T_{amb} are the adiabatic and ambient temperature respectively; and a_i and b_i are thermodynamic constant given in $J.mol^{-1}K^{-1}$ (available from electronic databases and handbook such as JANAF thermochemical tables). Equation (7) is adapted from Flagan and Seinfeld (2012).

For this model, the typical range of adiabatic temperatures obtained for various fuel compositions fall in the range 1900 - 2440 K. Use of equations (6) and (7) means that a further input parameter, T_{amb}, must be supplied. The appearance of ambient temperatures in equations (6) and (7) is also the first appearance of environmental condition in the problem, indicating that the geographical context of flaring may be significant in determining emission factors.

To fully relate the soot yield in Fig. 1 to our proposed input parameters (x, y, ϕ, T_{amb}), it is necessary to consider the difference between the test flame in the study by McEwen and Johnson relative to real-world gas flares. It should be noted that the chemistry of soot depend sensitively on the composition of the fuel (Kostiuk *et al.*, 2004) and fuel gas with high carbon to hydrogen ratio has a greater tendency to smoke (Akeredolu and Sonibare, 2004). The fuel used in McEwen and Johnson (2012) is made up of four alkane species (CH_4, C_2H_6, C_3H_8 and nC_4H_{10}) with methane (CH_4) being 85.24 % by volume of the fuel gas. The carbon to hydrogen ratio of the fuel used by McEwen and Johnson (2012) is ~0.25, a value less than 0.27 - 0.29 for typical fuel composition in real-world gas flares (Fawole *et al.,* 2016).

Soot scaling parameter

Lab-based study of emissions from flares is the most common and readily available method to estimate emissions from full-scale flares. Considering the size (diameter) of stack, higher fuel flow flux, and invariably the flue gas exit velocity of full-scale flares, there is the need to apply a scaling parameter to lab-based flare emission yields in order to estimate the yield from a full-scale flare (Fawole *et al.,* 2016). In previous studies, Richardson ratio (Becker and Liang, 1982), flame length (Schug *et al.*, 1980) and Damkohler ratio (characteristic residence time) (Sivathanu and Faeth, 1990) are parameters that have been considered for such scaling purposes.

In the present work, the Richardson ratio, Ri_L, is used to scale up the soot yield data from the lab-based study by McEwen and Johnson (2012). Richardson ratio Ri_L, as defined by Becker and Liang (1982) (eq. 8) was adopted because it involves the buoyancy of the flame which is a parameter also considered in fire Froude number, Fr_f. Ri_L also has a good correlation with soot emission from propane flame (Becker and Yamazaki, 1978).

$$\mathrm{Ri_L} = \frac{\text{buoyancy of flame}}{\text{source momentum flux}} \cong \frac{\pi g \rho_\infty L^3}{\rho_e A V_e^2} \qquad (8)$$

where L - flame length (m)

g – acceleration due to gravity (m/s^2)

A – cross-sectional area of stack (m^2)

V_e – flue gas exit velocity (m/s)

ρ_∞, ρ_e – density of ambient air and flue gas, respectively (kg/m^3)

Ri_L varies with fuel composition as a result of the dependence of flame length, L, on the net heat released by the fuel during combustion.

For $Fr_f = 0.005$, the soot yield in the experiment by McEwen and Johnson (2012) is 0.42 g of soot/kg of fuel burned (see Fig.1). For the same value of Fr_f the scaled-up values of soot yield are 0.79 and 1.11 g of soot/kg of fuel burned for fuel compositions I and II, respectively. The model calculates the fire Froude number, Fr_f from the inputs (x, y, ϕ, T_{amb}, ρ_a, g, d_e) supplied by the user. The calculated Fr_f is used to estimate total soot yield from the scaled-up experimental soot yield data.

If, for the sake of simplicity and in the absence of a more process-based structural relationship, we assume that the soot yield per component, x_i, of a fuel mix of n hydrocarbon components is simple linear function of the contribution of hydrocarbon i to the overall (non-CO_2) carbon budget, then we have:

$$\chi_i = \frac{C_i F_i}{\sum_{j=1}^{n} C_j F_j} \cdot S_i \cdot \chi_{Tot} \qquad (9)$$

In Eq. (9), C_i is the number of carbon atoms in the empirical formula of component *I*, F_i is the volume fraction of component *I*, and X_{Tot} is the total soot yield from the flame. The parameter S_i is a dimensionless empirical function (such as the Richardson ratio described above) which accounts for the greater propensity of a full-scale flare to soot as a result of the stack size, flame characteristics and fuel gas flow characteristics.

RESULTS AND DISCUSSION

Soot Yield

The two fuel compositions given in Table 1 have been used to evaluate the effect of fuel composition of the EFs. Other parameters such as the fuel gas densities and molar masses are also provided in Table 1. The ambient temperature (298 K), stack diameter (0.75 m) and atmospheric pressure (1.0133×10^5 Pa) are kept constant during the calculation.

Table 1: Fuel compositions used in this study (given in molar percentage)

	I	II
CH_4	88.72	69.58
C_2H_6	5.93	0.25
C_3H_8	1.28	12.54
nC_4H_{10}	0.26	2.35
iC_4H_{10}	0.26	5.12
nC_5H_{12}	0.06	5.20
iC_5H_{12}	0.09	2.54
C_6H_{14}	0.06	1.97
C_7H_{16}	0.1	-
N_2	0.66	0.24
CO_2	2.55	0.21
H_2S	0.03	-
C : H	0.25	0.29
HHV* (kJ/mol)	939.8	1480.4
Molar mass (g/mol)	18.5	28.6
Density (kg/m^3)	0.75	1.2

* Higher (gross) Heating Value of the fuel gas

For fuel composition I, at ϕ = 1.0, the fire Froude number Fr_f = 0.0045. Scaling down the soot yields for each hydrocarbon species in the fuel gas by their percentage molar concentration in the fuel gas, gives a total soot yield of 0.0143 g/mol of the fuel gas under the conditions stated above.

EF_{soot} = total soot yield (g/mol) x molar density of fuel (mol/m^3)

Hence, estimated EF_{soot} = 0.58g/m^3 (equivalent to 0.00076 kg of soot/kg of fuel burned). And, for a flow flux = 1.174 m^3/s , the soot emission rate (ER) is 0.69 g/s.

For fuel composition II under the same condition, the estimated Ef_{soot} = 1.73 g/m^3. This is equivalent to 0.0015 kg of soot/ kg of fuel burned and an emission rate of 2.03 g/s for the same fuel flow flux.

In the estimation proposed in this work, the percentage of carbon content of the fuel gas that ends up as soot for 0.8 ≤ ϕ ≤ 1.3 ranges between 0.1 and 0.35 % (by mass) which is in consonance with less than 0.4 % found out by Kostiuk et al. (2004) in their pilot study carried out in the University of Alberta, Canada. The CCE for the various fire and fuel characteristics used in this study is between 99.5 and 33.7 % (see Figures 4 and 5 for the variation of CCE with ϕ).

Carbon monoxide yield

For a fuel gas made up of N alkane species, the emission factor for carbon monoxide (EF_{CO}) is estimated as:

$$EF_{co} = \frac{n_{co}}{n_{fuel\ gas}} \frac{PM_{co}}{RT} \qquad (10)$$

where $\frac{n_{co}}{n_{fuel\ gas}} = \Sigma_i^N q_i c_i$

P – atmospheric pressure (Pa)
R – universal gas constant (m^{3}Pa/K.mol)
M_{CO} – molar masses of CO (g/mol)
T – ambient temperature (K)
q_i and c_i - the CO yield and percentage molar concentration of species ***i*** in the fuel gas.

Under the combustion conditions given above for soot, for fuel gas composition I

$$\frac{n_{CO}}{n_{fuel\ gas}} = 0.0054$$

By eq. (10), this gives EF_{CO} = 6.16 g/m^3 (equivalent to 0.0082 kg/kg of fuel burned). For fuel flow flux = 1.174 m^3/s, ER = 7.2x10^{-3} kg/s.
For composition II:

$$\frac{n_{CO}}{n_{fuel\ gas}} = 0.0093$$

Hence, EF_{CO} = 10.69 g/m^3 (equivalent to 0.0092 kg/kg of fuel burned and 1.3x10^{-2} kg/s).

Carbon dioxide yield

$$EF_{co2} = \frac{n_{co2}}{n_{fuel\ gas}} \frac{PM_{co2}}{RT} \qquad (11)$$

where $\frac{n_{co2}}{n_{fuel\ gas}} = \sum_i^N p_i c_i$

M_{CO2} – molar masses of CO_2 (g/mol)
pi and ci - the CO_2 yield and percentage molar concentration of species ***i*** in the fuel gas.

Under the combustion conditions given above, for fuel gas composition I:

$$\frac{n_{CO_2}}{n_{fuel\ gas}} = 1.10$$

By eq. (11), this gives EF_{CO2} = 1.98 kg/m^3 (equivalent to 2.62 kg/kg of fuel burned and 2.32 kg/s)
For composition II:

$$\frac{n_{CO_2}}{n_{fuel\ gas}} = 1.86;$$

Hence, EF_{CO2} = 3.35 kg/m^3 (equivalent to 2.87 kg/kg of fuel burned and 3.93 kg/s)

For the 10 different fuel gas compositions obtained from Sonibare and Akeredolu (2004), the relationships between their soot yield, molar masses and higher heating values (HHV) are presented in Fig. 2. The soot yields and HHV of these fuel gas compositions are estimated from this model for ϕ =1. It should be noted that HHV can only be calculated at ϕ =1 because HHV is the amount of heat given off by the complete combustion of a fuel. For these fuels, the range of the molar mass and HHV are 18 - 28.6 and 39.9 – 60.3, respectively.

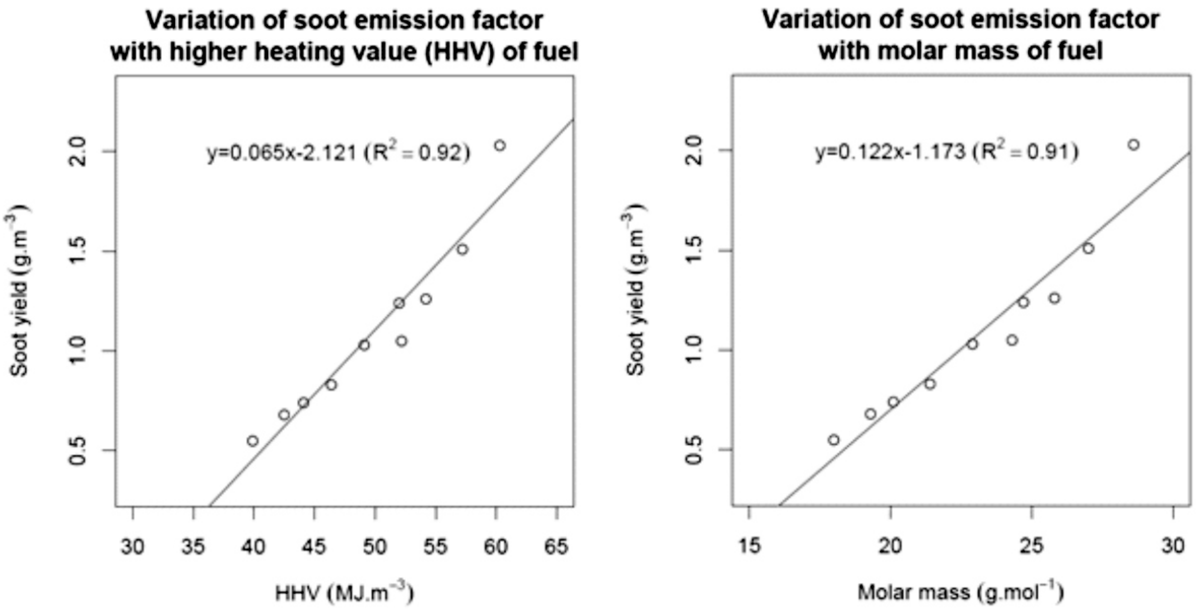

Figure 2: Relationship between EF_{soot}, molar mass and HHV for some fuel compositions

For this study, it is assumed that the carbon content of the fuel gas ends up as CO_2, CO and soot. Hence, eliminating the presence of PAH and other incompletely oxidized hydrocarbon from the loop. For the denser fuel composition (composition II), the variation of CO_2, CO and soot with equivalent ratio, ϕ is shown in Fig. 3a while Fig. 3b shows the variation of CO to CO_2 ratio with ϕ where the gradient gets steeper as ϕ increases but plateaued when $\phi < 1$.

A comparison of the EF estimates from this study with those obtained from similar study from literature – lab-based, pilot study, field measurement and calculations – are presented in Tables 2a and 2b. It should be noted, however, that this work considered two very different fuel compositions (light and dense). As such, two different EFs will be quoted for comparison in the tables below.

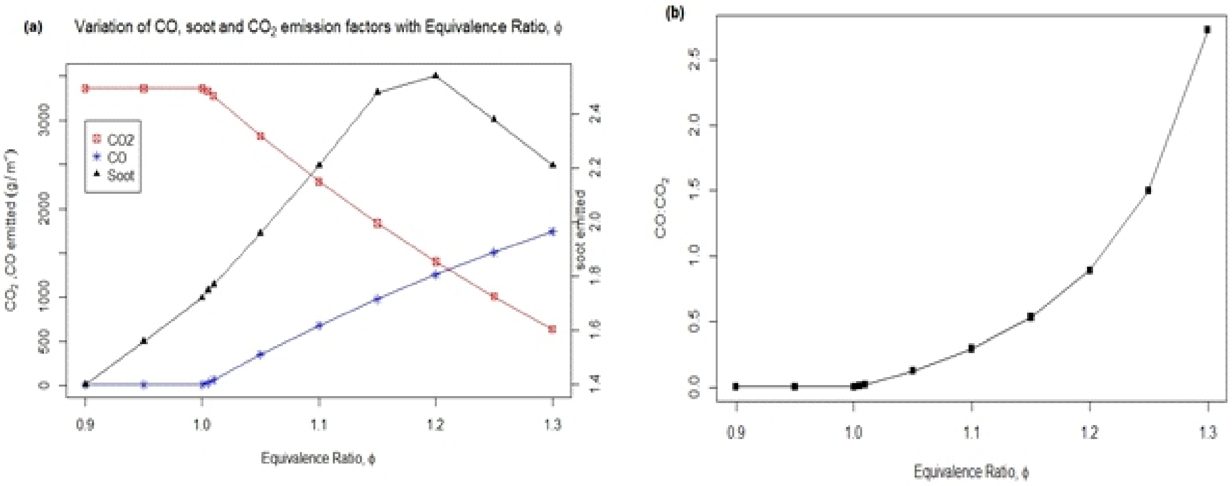

Figure 3: (a) Relationship between equivalence ratio (ϕ), EF_{CO2}, EF_{CO} and EF_{soot} (b) variation of CO:CO_2 with ϕ.

The method developed here produced EFs and emission rates (ERs) that compare favourably well with those obtained from similar studies in literature. ER is the product of EF (g/m^3) and fuel flow flux (m^3/s). Fuel flow flux varies significantly from one field to another and can be as high as 32.3 m^3/s, the estimated value for an active flare in Venezuela which is ranked #1 globally (Elvidge *et al.*, 2015). In this model, EF_{soot} of 0.58 and 1.73 g/m^3 obtained for fuel I and II, respectively, fall within the light- and averagely-smoking flare category for USEPA (1995). For soot, emission rates of 6.9 x 10^{-4} and 2.02 x 10^{-3} kg/s obtained for fuel I and II, respectively, compare well with those obtained in similar studies by IMP (2006) and Almanza et al. (2012). We have used fuel flow flux = 1.174 m^3/s for our estimations in this study. The values obtained for EF_{CO} and EF_{CO2} compare well with those from United Kingdom Offshore Association (UKOA), Talebi et al. (2014) and USEPA (1995).

Table 2a: Emission Factor (EF) for soot

Reference	EF ($kg/10^3m^3$ of fuel)	EF (kg/s)	Type of fuel
(USEPA, 1995)	0, 0.9, 4.2, 6.4	-	80% propylene 20% propane
(Johnson *et al*., 2013)	-	6.7 x10^{-5}	field measurement
(McEwen and Johnson, 2012)	0.51	-	85.2 % methane, 7.1% ethane, 2% propane, 1.4 % n-butane
(IMP, 2006) [a]	-	3.37 x 10^{-3}	-
(Almanza *et al.,* 2012)	-	2.24 x 10^{-4}	-
(Johnson *et al*., 2011)	-	2.0±0.66x10^{-3}	-
GAINS (Stohl *et al.,* 2013)	1.6	-	modelling
This work - Fuel I	0.58	6.9 x 10^{-4}	associated gas
Fuel II	1.73	2.02 x 10^{-3}	associated gas

[a] quoted from Almanza et al. (2012)

Table 2b: Emission factors for carbon monoxide and carbon dioxide

References	CO (kg/kg)	CO_2 (kg/kg)	CO (kg/s)	CO_2 (kg/s)	CO (kg/GJ)	CO_2 (kg/GJ)
(EEMS, 2008)	0.0067	2.8	-	-	-	-
(USEPA, 1995)	-	-	-	-	0.16	50.2
The Norwegian Oil Industry Association [b]	-	-	-	-	0.026	63.6
(Talebi *et al*., 2014)	-	-	-	-	0.1 –0.59	49.0-51.6
United Kingdom Offshore Association (UKOA) [b]	-	-	-	-	0.26	61.8
This work (fuel I)	0.0082	2.62	0.007	2.32	0.24	69.23
This work (fuel II)	0.0092	2.87	0.013	3.93	0.26	74.3

[b] quoted from Talebi et al. (2014).

The graphs in Figures 4 and 5 show the 2-dimensional variation of EF_{soot}, EF_{CO} and EF_{CO2} with equivalence ratio, ϕ and flue gas exit velocity, V_s. The graphs also show the variation of CCE with ϕ for the two fuel compositions used in this study. The exit velocity of the flue gas was varied by varying the volume flux (m^3/s) of the fuel gas while the stack diameter is kept constant. Soot given off is dependent on both the equivalent ratio and the flame dynamics characteristics as measured by the fire Froude number. Low values of V_s, (for example, 2.0 m/s) can produce very sooty flames at higher values of ϕ. At high flue gas exit velocity (> 6m/s) and high ϕ (> 1.1), the low value of soot emitted is probably due to some of the fuel 'escaping' unburned as a result of the high exit velocity and low amount of oxygen available (see Figs. 4 and 5).

The heavier the fuel gas the more oxygen needed for combustion. The molar masses of fuel compositions I and II are 18.5 and 28.6, respectively. A difference of 0.04 in the value of C:H for fuel composition I and II results in an increase of EF_{soot}, EF_{CO} and EF_{CO2} by factors of ~3, ~1.4 and ~1.7, respectively. This underpins the importance of fuel composition in the estimation of pollutants emission from the combustion of hydrocarbons. The importance of a qualitative idea of the amount of air available for the combustion, the fuel gas flow rate and stack characteristics (diameter) are also demonstrated with the wide variation of emission quantities.

These emission factor (EF) estimations (CO, CO_2, soot) have been coded into MATLAB as a pre-processor for dispersion modeling software. The user supplies the fuel composition (preferably, in percentage molar composition), equivalence ratio (ϕ), ambient temperature, atmospheric pressure, stack diameter and fuel gas flow flux (m^3/s). The pre-processor generates estimates for the yields of soot, CO_2, and CO. Other combustion parameters generated by the pre-processor are flame length (m), net heat released (MJ/s) and flue gas exit velocity (m/s).

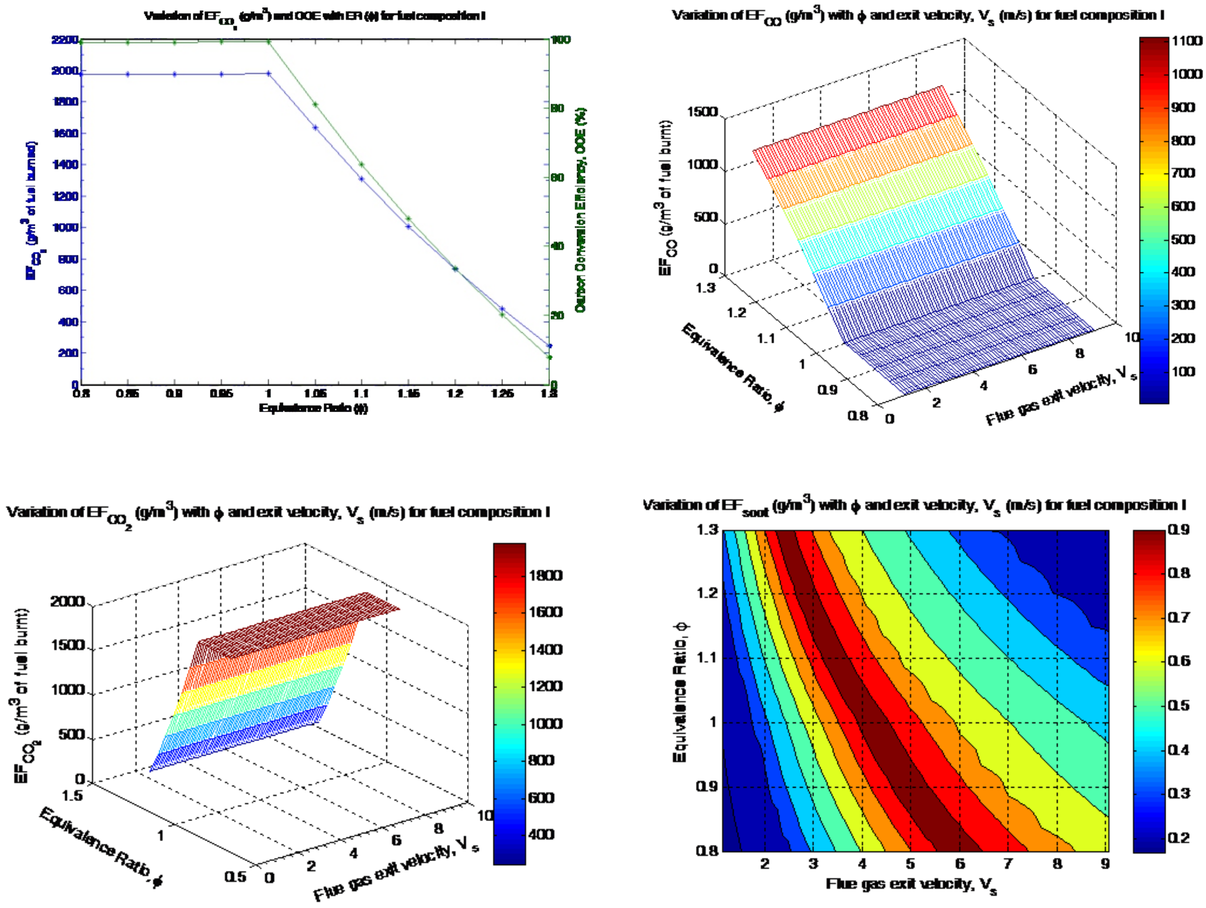

Figure 4: Variation of CCE, CO_2, CO and soot yields with ϕ and flue gas exit velocity for fuel composition I.

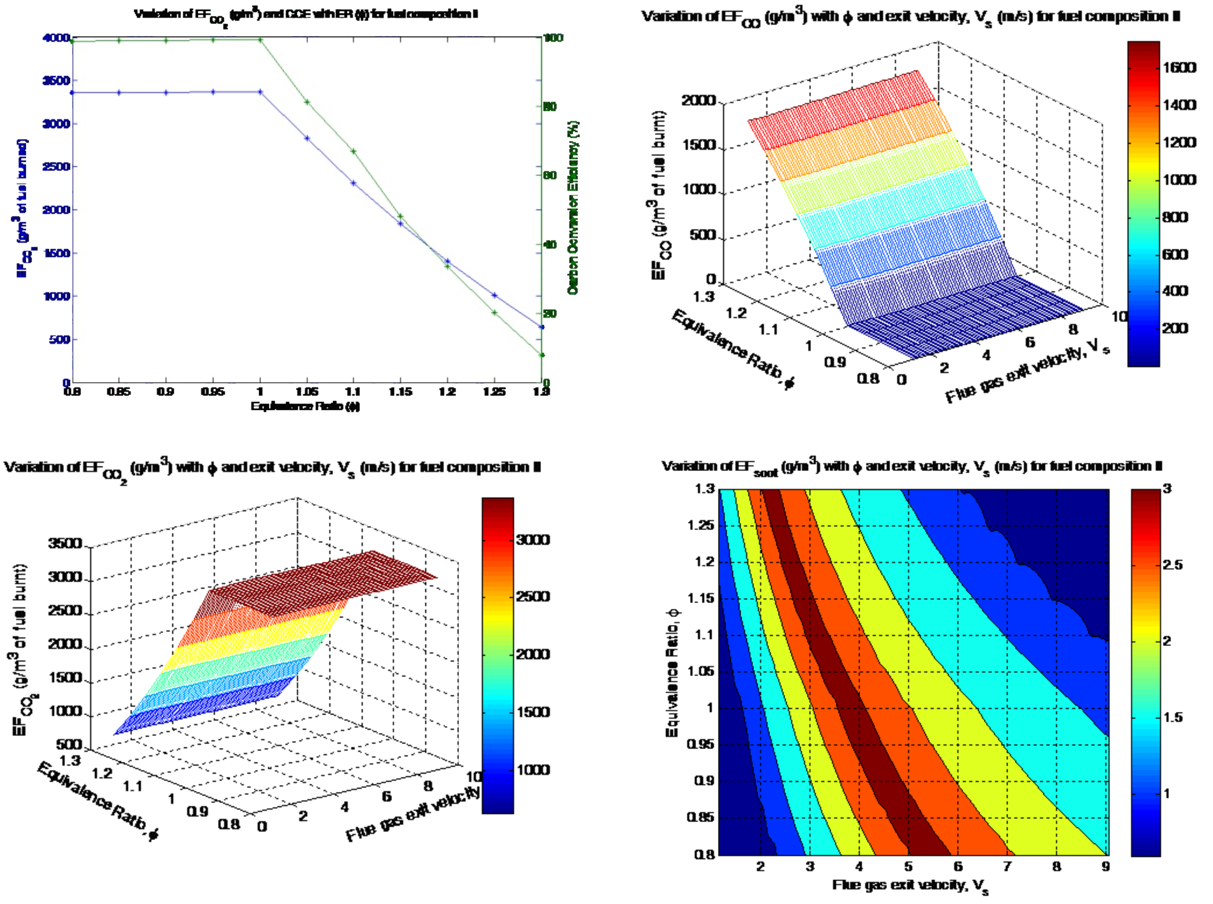

Figure 5: Variation of CCE, CO_2, CO and soot yields with ϕ and exit velocity for fuel composition II.

CONCLUSION

This work developed a simple self-consistent technique to estimate the emission factors of carbon-containing emissions from a typical gas flare. The technique factors in the effect of fuel composition and flame dynamics characteristics. The dependence of pollutants emission on fuel gas composition, fuel flow flux, stack characteristics and equivalence ratio, ϕ, were demonstrated using two fuel gases of varying composition. The mass-weighted carbon to hydrogen ratio (C:H) of fuel gas, a function of the fuel composition, plays a very prominent role in the nature and quantity of pollutants emitted from the combustion process. The use of generalized emission factors for carbon-containing pollutants emitted from gas flares, a highly varying source of pollutants, could be responsible for the disparities in model simulations and measurements in prominent gas flaring regions of the world.

The estimates from this pre-processor can be further validated and improved upon by more elaborate field measurements from gas flaring sites rather than lab-based or pilot-scale studies. It (pre-processor) could be made more accurate when other experimental works can provide similar data to better constrain '*rC*' Presently, the study by McEwen and Johnson is the only known study that can be applied directly in our proposed estimation technique. Experimental work that gives soot yield from hydrocarbon, typically alkane, combustion as a function of a combustion (fuel or flame) dynamics parameter is quite suitable for the method proposed here. The pre-processor developed in this study finds application in the oil and gas industry. It can support the work of environmental officers in the oil and gas industry to estimate pollutants emission for the combustion of associated gas, especially in typical 'real world' gas flares.

ACKNOWLEDGEMENT

Olusegun G. Fawole is highly grateful to the UK

Department for International Development (DFID) for funding his PhD studies through the UK Commonwealth Scholarships Commission (CSCUK) NGCA-2013-70.

REFERENCES

Abdulkareem, A.S., Afolabi, A.S., Jimoh, A., Uthman, H. and Odigure, J., 2012. Oil Exploration and Climate Change: A Case Study of Heat Radiation from Gas Flaring in the Niger Delta Area of Nigeria. INTECH open science, Chapter 1.

Akeredolu, F. and Sonibare, J., 2004. A review of the usefulness of gas flares in air pollution control. Management of Environmental Quality: An International Journal, 15(6): 574-583.

Almanza, V., Molina, L. and Sosa, G., 2012. Soot and SO 2 contribution to the supersites in the MILAGRO campaign from elevated flares in the Tula Refinery. *Atmospheric Chemistry and Physics*, 12(21): 10583-10599.

Becker, H. and Liang, D., 1982. Total emission of soot and thermal radiation by free turbulent diffusion flames. *Combustion and Flame*, 44(1): 305-318.

Becker, H. and Yamazaki, S., 1978. Entrainment, momentum flux and temperature in vertical free turbulent diffusion flames. *Combustion and Flame*, 33: 123-149.

Beychok, M.R., 1994. Fundamentals of stack gas dispersion, 63. Milton R. Beychok Irvine.

Bishop, G. and Stedman, D., 1996. Measuring the emissions of passing cars. *Accounts of Chemical Research*, 29(10): 489-495.

Bond, T.C., Doherty, S.J., Fahey, D., Forster, P., Berntsen, T., DeAngelo, B., Flanner, M., Ghan, S., Kärcher, B. and Koch, D., 2013. Bounding the role of black carbon in the climate system: A scientific assessment. *Journal of Geophysical Research: Atmospheres*, 118(11): 5380-5552.

Bourguignon, E., Johnson, M. and Kostiuk, L., 1999. The use of a closed-loop wind tunnel for measuring the combustion efficiency of flames in a cross flow. *Combustion and flame*, 119(3): 319-334.

Canteenwalla, P., Thomson, K., Smallwood, G. and Johnson, M., 2007. Soot emissions from turblent diffusion flames burning simple alkane fuels. http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/ctrl?action=shwart&index=an&req=8894822&lang=en (last accessed on February 19, 2015)

Castineira, D. and Edgar, T.F., 2006. CFD for simulation of steam-assisted and air-assisted flare combustion systems. *Energy & fuels*, 20(3): 1044-1056.

Chow, J.C., Watson, J.G., Lu, Z., Lowenthal, D.H., Frazier, C.A., Solomon, P.A., Thuillier, R.H. and Magliano, K., 1996. Descriptive analysis of PM2.5 and PM10 at regionally representative locations during SJVAQS/AUSPEX. *Atmospheric Environment*, 30(12): 2079-2112.

Delichatsios, M., 1993. Transition from momentum to buoyancy-controlled turbulent jet diffusion flames and flame height relationships. *Combustion and flame*, 92(4): 349-364.

Djuricin, S., Pataki, D.E. and Xu, X., 2010. A comparison of tracer methods for quantifying CO2 sources in an urban region. *Journal of Geophysical Research: Atmospheres* (1984-2012), 115(D11).

Edwards, P.M., Brown, S.S., Roberts, J.M., Ahmadov, R., Banta, R.M., deGouw, J.A., Dube, W.P., Field, R.A., Flynn, J.H., Gilman, J.B., Graus, M., Helmig, D., Koss, A., Langford, A.O., Lefer, B.L., Lerner, B.M., Li, R., Li, S.-M., McKeen, S.A., Murphy, S.M., Parrish, D.D., Senff, C.J., Soltis, J., Stutz, J., Sweeney, C., Thompson, C.R., Trainer, M.K., Tsai, C., Veres, P.R., Washenfelder, R.A., Warneke, C., Wild, R.J., Young, C.J., Yuan, B. and Zamora, R., 2014. High winter ozone pollution from carbonyl photolysis in an oil and gas basin. Nature, advance online publication.

EEA, 2006. Waste incineration: Flaring in gas and oil extraction, Emission Inventory Guidebook, European Environment Agency, Copenhagen, Denmark.

EEMS, 2008. Atmospheric emissions calculations, Environmental Emissions Monitoring System, United Kingdom.

Elvidge, C.D., Zhizhin, M., Baugh, K., Hsu, F.-C. and Ghosh, T., 2015. Methods for Global Survey of Natural Gas Flaring from Visible Infrared Imaging Radiometer Suite Data. *Energies*, 9(1): 14.

Fawole, O., Cai, X.-M. and MacKenzie, A., 2016. Gas flaring and resultant air pollution: A review focusing on Black Carbon. Environmental Pollution, 216: 182-197. doi: 10.1016/j.envpol.2016.05.075.

Fawole, O.G., Cai, X. and MacKenzie, A., 2017. Evidence for a gas-flaring source of alkanes leading to elevated ozone in air above West Africa. *African Journal of Environmental Science and Technology*, 11(10): 532-543.

Feichter, J. and Stier, P., 2012. Assessment of black carbon radiative effects in climate models. *Wiley Interdisciplinary Reviews: Climate Change*, 3(4): 359-370.

Flagan, R.C. and Seinfeld, J.H., 2012. Fundamentals of air pollution engineering. Courier Dover Publications.

Fortner, E., Brooks, W., Onasch, T., Canagaratna, M., Massoli, P., Jayne, J., Franklin, J., Knighton, W., Wormhoudt, J. and Worsnop, D., 2012. Particulate Emissions Measured During the TCEQ Comprehensive Flare Emission Study. *Industrial & Engineering Chemistry Research*, 51(39): 12586-12592.

GGFR, 2012. Estimated Flared Volumes from Satellite Data, 2007-2011., Global Gas Flaring Reduction, http://go.worldbank.org/G2OAW2DKZ0 (last accessed on January 9, 2015).

Gilman, J., Lerner, B., Kuster, W. and De Gouw, J., 2013. Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado. *Environmental science & technology*, 47(3): 1297-1305.

Huang, K., Fu, J.S., Prikhodko, V.Y., Storey, J.M., Romanov, A., Hodson, E.L., Cresko, J., Morozova, I., Ignatieva, Y. and Cabaniss, J., 2015. Russian anthropogenic black carbon: Emission reconstruction and Arctic black carbon simulation. *Journal of Geophysical Research: Atmospheres*, 120. 10.1002/2015JD023358.

IEA, 2012. IEA statistics: Natural gas information, International Energy Agency, Paris, France.

IMP, 2006. Estudio de las emisiones de la zona industrial de Tula y su impacto en la calidad del aire regional , PS-MA-IF-F21393-1, IMP, Mexico.

Ismail, O.S. and Umukoro, G.E., 2016. Modelling combustion reactions for gas flaring and its resulting emissions. *Journal of King Saud University-Engineering Sciences*, 28(2): 130-140.

Jacobson, M.Z., 2002. Control of fossil?fuel particulate black carbon and organic matter, possibly the most effective method of slowing global warming. *Journal of Geophysical Research: Atmospheres* (1984-2012), 107(D19): ACH 16-1-ACH 16-22.

Johnson, M., Devillers, R. and Thomson, K., 2013. A Generalized Sky-LOSA Method to Quantify Soot/Black Carbon Emission Rates in Atmospheric Plumes of Gas Flares. *Aerosol Science and Technology*, 47(9): 1017-1029.

Johnson, M. and Kostiuk, L., 2000. Efficiencies of low-momentum jet diffusion flames in crosswinds. *Combustion and Flame*, 123(1): 189-200.

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. *Environmental science & technology*, 45(1): 345-350.

Kirchstetter, T.W., Harley, R.A., Kreisberg, N.M., Stolzenburg, M.R. and Hering, S.V., 1999. On-road measurement of fine particle and nitrogen oxide emissions from light- and heavy-duty motor vehicles. *Atmospheric Environment*, 33(18): 2955-2968.

Kostiuk, L., Johnson, M. and Thomas, G., 2004. University Of Alberta Flare Research Project: final report November 1996-September 2004. 2, http://www.mece.ualberta.ca/groups/combustion/flare/papers/Final%20Report2004.pdf.

Leahey, D.M., Preston, K. and Strosher, M., 2001. Theoretical and observational assessments of flare efficiencies. *Journal of the Air & Waste Management Association*, 51(12): 1610-1616.

Li, C., Hsu, N.C., Sayer, A.M., Krotkov, N.A., Fu, J.S., Lamsal, L.N., Lee, J. and Tsay, S.-C., 2016. Satellite observation of pollutant emissions from gas flaring activities near the Arctic. *Atmospheric Environment*, 133: 1-11.

Liousse, C., Keita, S., Granier, L., Granier, C., Elvidge, C.D., Elguindi, N. and Law, K., 2019. Flaring emissions in Africa: Distribution, evolution and comparison with current inventories. *Atmospheric environment*, 199: 423-434.

McAllister, S., Chen, J.-Y. and Fernandez-Pello, A.C., 2011. Fundamentals of combustion processes. Springer.

McDaniel, M. and Tichenor, B.A., 1983. Flare efficiency study, US Environmental Protection Agency, Industrial Environmental Research Laboratory, http://www.tceq.state.tx.us/assets/public/implementation/air/rules/Flare/Resource_1.pdf.

McEwen, J.D. and Johnson, M.R., 2012. Black carbon particulate matter emission factors for buoyancy-driven associated gas flares. *Journal of the Air & Waste Management Association*, 62(3): 307-321.

Obanijesu, E., Adebiyi, F., Sonibare, J. and Okelana, O., 2009. Air-borne SO2 Pollution Monitoring in the Upstream Petroleum Operation Areas of Niger-Delta, Nigeria. *Energy Sources*, Part A, 31(3): 223-231.

Ramana, M., Ramanathan, V., Feng, Y., Yoon, S., Kim, S., Carmichael, G. and Schauer, J., 2010. Warming influenced by the ratio of black carbon to sulphate and the black-carbon source. *Nature Geoscience*, 3(8): 542-545.

Ramanathan, V. and Carmichael, G., 2008. Global and regional climate changes due to black carbon. *Nature Geoscience*, 1(4): 221-227.

Santos, F., Fraser, M. and Bird, J., 2014. Atmospheric black carbon deposition and characterization of biomass burning tracers in a northern temperate forest. *Atmospheric Environment*, 95: 383-390.

Schug, K., Manheimer-Timnat, Y., Yaccarino, P. and Glassman, I., 1980. Sooting behavior of gaseous hydrocarbon diffusion flames and the influence of additives. *Combustion Science and Technology*, 22(5-6): 235-250.

Schwarz, J.P., Holloway, J.S., Katich, J.M., McKeen, S., Kort, E.A., Smith, M.L., Ryerson, T.B., Sweeney, C. and Peischl, J., 2015. Black carbon emissions from the Bakken Oil and Gas Development region. *Environmental Science & Technology Letters*, 2(10): 281-285.

Seinfeld, J., 2008. Atmospheric science: Black carbon and brown clouds. *Nature Geoscience*, 1(1): 15-16.

Siegel, K., 1980. Degree of conversion of flare gas in refinery high flares, Thesis PhD in Engr. Science, Chemical Engr. Dept., Univ. of Karlesruhe, Germany (February, 1980).

Sivathanu, Y. and Faeth, G.M., 1990. Soot volume fractions in the overfire region of turbulent diffusion flames. *Combustion and Flame*, 81(2): 133-149.

Sonibare, J., Adebiyi, F., Obanijesu, E. and Okelana, O., 2010. Air quality index pattern around petroleum production facilities. *Management of Environmental Quality: An International Journal*, 21(3): 379-392.

Sonibare, J.A. and Akeredolu, F.A., 2004. A theoretical prediction of non-methane gaseous emissions from natural gas combustion. *Energy Policy*, 32(14): 1653-1665.

Stohl, A., Klimont, Z., Eckhardt, S., Kupiainen, K., Shevchenko, V., Kopeikin, V. and Novigatsky, A., 2013. Black carbon in the Arctic: the underestimated role of gas flaring and residential combustion emissions. *Atmospheric Chemistry and Physics*, 13(17): 8833-8855.

Stone, D.K., Lynch, S.K., Pandullo, R.F., Evans, L.B. and Vatavuk, W.M., 1992. Flares. Part I: Flaring Technologies for Controlling VOC-Containing Waste Streams. *Journal of the Air & Waste Management Association*, 42(3): 333-340.

Strosher, M.T., 2000. Characterization of emissions from diffusion flare systems. *Journal of the Air & Waste Management Association*, 50(10): 1723-1733.

Talebi, A., Fatehifar, E., Alizadeh, R. and Kahforoushan, D., 2014. The Estimation and Evaluation of New CO, CO2, and NOx Emission Factors for Gas Flares Using Pilot Scale Flare. *Energy Sources*, Part A: Recovery, Utilization, and

Environmental Effects, 36(7): 719-726.

Tegen, I., Hollrig, P., Chin, M., Fung, I., Jacob, D. and Penner, J., 1997. Contribution of different aerosol species to the global aerosol extinction optical thickness: Estimates from model results. *Journal of Geophysical Research: Atmospheres* (1984-2012), 102(D20): 23895-23915.

Torres, V.M., Herndon, S. and Allen, D.T., 2012a. Industrial flare performance at low flow conditions. 2. Steam-and air-assisted flares. *Industrial & Engineering Chemistry Research*, 51(39): 12569-12576.

Torres, V.M., Herndon, S., Kodesh, Z. and Allen, D.T., 2012b. Industrial flare performance at low flow conditions. 1. Study overview. *Industrial & Engineering Chemistry Research*, 51(39): 12559-12568.

USEPA, 1995. AP 42-Compilation of air pollutant emission factors. Section 13.5: Industrial flares, U.S Environmental Protection Agenecy, Office of Air quality planning and standards, Research Triangle Park, NC. http://www.epa.gov/ttn/chief/ap42/ch13/final/c13s05.pdf.

USEPA, 2014. AP 42-Compilation of air pollutant emission factors. Section 13.5: Industrial flares, U.S Environmental Protection Agenecy, Office of Air quality planning and standards, Research Triangle Park, NC.

Weyant, C.L., Shepson, P.B., Subramanian, R., Cambaliza, M.O., Heimburger, A., McCabe, D., Baum, E., Stirm, B.H. and Bond, T.C., 2016. Black carbon emissions from associated natural gas flaring. *Environmental Science & Technology*, 50(4): 2075-2081.