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ORIGINAL ARTICLES Modelling emissions from natural gas flaring

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KEYWORDS

Modelling; Emissions; Natural gas; Environmental degradation; Gas flaring; Combustion **Abstract** The world today recognizes the significance of environmental sustainability to the development of nations. Hence, the role oil and gas industry plays in environmental degrading activities such as gas flaring is of global concern. This study presents material balance equations and predicts results for non-hydrocarbon emissions such as CO_2 , CO, NO, NO_2 , and SO_2 etc. from flaring (combustion) of 12 natural gas samples representing composition of natural gas of global origin. Gaseous emission estimates and pattern were modelled by coding material balance equations for six reaction types and combustion conditions with a computer program. On the average, anticipated gaseous emissions from flaring natural gas with an average annual global flaring rate 126 bcm per year (between 2000 and 2011) in million metric tonnes (mmt) are 560 mmt, 48 mmt, 91 mmt, 93 mmt and 50 mmt for CO_2 , CO, NO, NO_2 and SO_2 respectively. This model predicted gaseous emissions based on the possible individual combustion types and conditions anticipated in gas flaring operation. It will assist in the effort by environmental agencies and all concerned to track and measure the extent of environmental pollution caused by gas flaring operations in the oil and gas industry.

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1. Introduction

'Flare the gas, flare the environment,' a cliché one can quickly use to discourage gas flaring. Flaring has been described as a multibillion dollar waste and a local environmental catastrophe. However, it is still widely used as a disposal option for associated gas in oil production especially where there is inad-

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equate infrastructure for utilization of this gas. This is because flaring minimizes venting and can also burn efficiently. Environmental issues of gas flaring are generally described in terms of efficiency and emissions (Gobo et al., 2009). Flaring can be inefficient especially with combustion being affected by ambient winds and several other factors leading to incomplete combustion. Incomplete combustion leads to formation of several products resulting from various reactions taking place. Li and Williams (1999), gave several reactions taking place in combustion of natural gas. During a combustion reaction, several intermediate products are formed, and eventually, most of them are converted to CO₂ and water. Some stable intermediate products and other by-products such as hydrocarbons, CO, H₂, NO, NO₂, SO₂ etc. will escape as emissions (Kahforoshan et al., 2008; AbdulKareem et al., 2009). The effect of thermal radiation emitted from flaring operation is also of great

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concern, as there are limits to which the habitat can tolerate the fluxes released (Ismail and Fagbenle, 2009).

One of the challenges involved in addressing environmental aspects of flaring is determining how much emission is being released. Several methods exist for quantifying emissions, including direct measurement of sources and estimation techniques such as emission factors and engineering calculations. Direct measurement involves measuring actual emissions and collecting empirical data from a source or process. Emission factors are representative values that relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant, while engineering calculations refer to the estimation of emissions using engineering parameters (EPA, 2013). Some of these methods were reviewed in (Ismail and Umukoro, 2012). Marland and Rotty (1984), for example, estimated the amount of CO₂ emitted to the atmosphere from fossil-fuel burning, gas flaring, and cement production using Eq. (1).

$$CO_2 i = (Pi)(FOi)(Ci)$$
 (1)

where subscript i represents a particular fuel commodity, P represents the amount of fuel i that is consumed each year, FO is the fraction of P that is oxidized, C is the average carbon content for fuel i, and CO_2 is the resulting CO_2 emissions for fuel i expressed in mass of carbon. Global total CO_2 emission estimates are generated by using the above equation, where P represents production data from the United Nations Statistic Database for all primary solid, liquid, and gas fuels (Boden et al., 1995).

There has been continuous effort to improve on some of these methods. Estimation for example is unsure and uncertain as they are based on experiments in controlled environment and assumptions of certain factors. Also, some emission factors in use are questionable. The EPA for example, has no emission factor for flares and enclosed combustors for NOx, CO, SO₂ and some greenhouse gas (EPA, 2013). With predictive models and combustion analysis such as the one attempted here, better prediction of emissions that degrade our environment can be made in order to meet federal, state and local environmental regulations. This paper presents an attempt at a prediction of the emissions of CO, CO_2 , NO, NO_2 , and SO_2 from the flaring of associated natural gas.

2. Methodology

Emission from gas flares is predicted here by adopting mass balance equations for various flaring conditions as developed in Ismail and Umukoro (2014). The 6 reaction types and conditions are presented here in Eqs. (2)–(9). All conditions considered favour incomplete combustion. The chemical composition of flared gas (Table 1) and combustion efficiency (measure of how effective that flare is in converting all of the carbon in the fuel to CO_2) are central in the analysis.

I. Reaction type 1: Incomplete combustion of "sweet gas" without the formation of oxides of nitrogen (NOx) at temperature T < 1200 Kelvin (K).

$$\begin{aligned} & [C_x H_y + a CO_2 + jN_2] + b(O_2 + 3.76N_2) \to \\ & \eta x CO_2 + \eta \frac{y}{2} H_2 O + (1 - \eta) x CO + (1 - \eta) \frac{y}{2} H_2 + dO_2 \\ & + jN_2 + a CO_2 + 3.76bN_2 \end{aligned}$$

where

$$d = \left[x\left(\frac{1}{2} - \frac{\eta}{2}\right) + y\left(\frac{1}{2} - \frac{\eta}{4}\right)\right] \tag{3}$$

'*a*' is the known stoichiometric coefficient for CO_2 in flare stream (Table 1).

b is the unknown stoichiometric coefficient for the amount of air involved in combustion.

'j' is the known stoichiometric coefficient for N_2 in flare stream (Table 1).

 C_xH_y is the total hydrocarbon in the composition of Natural gas (Table 1) and

d is the unknown stoichiometric coefficient for the excess oxygen in product of combustion.

' η ' is the combustion efficiency (mass based) expressed in terms of the stoichiometric coefficient.

II. Reaction type 2: Incomplete combustion of "sweet gas" with oxides of nitrogen (NO_x) formed as nitric oxide (NO) only. Reaction temperature (T) in kelvin is assumed to be $1200 \text{ K} \ge T \le 1600 \text{ K}$.

Table 1	Natural g	gas composit	ion in percen	tage moles/v	volume employed in	the study	•			
S/N	Methane	Ethane	Propane	Butane	Pentane (C_5+)	N_2	CO_2	H_2S	Gas field	Origin
1	92.51	2.78	1.66	0.78	0.30	0.11	0.22	-	Soku	Nigeria
2	90.12	6.94	2.09	0.771	0.079	-	-	-	FS-2	Nigeria
3	81.3	2.9	0.4	0.1	0.1	14.3	0.9	-	Groningen	(NLD)
4	95.7	3.6	-	-	-	0.4	0.3	-	Frigg	(NOR)
5	83.7	6.8	2.1	0.8	0.4	5.8	0.2	-	Hassi R'Mel	Algeria
6	85.3	5.8	5.3	2.1	0.2	0.9	0.4	-	Urengoy	Russia
7	45.6	5.8	2.9	1.1	0.8	-	43.8	-	Kapumi	(NZL)
8	82	10	3.7	1.9	0.7	1.5	0.2	-	Maracalbo	(VEN)
9	69	3	0.9	0.5	0.5	1.5	9.3	15.3	Lacq	France
10	55.5	18	9.8	4.5	1.6	0.2	8.9	1.5	Uthmaniyah	(SAU)
11	74.3	14	5.8	2	0.9	2.9	-	0.1	Burgan	Kuwait
12	56.9	21.2	6	3.7	1.6		7.1	3.5	Kirkuk	(IRQ)

Source: Ismail and Umukoro (2014).

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(4)

Modelling emissions from natural gas flaring

$$\begin{aligned} & [C_x H_y + a CO_2 + jN_2] + b(O_2 + 3.76N_2) \to \\ & \eta x CO_2 + \eta \frac{y}{2} H_2 O + (1 - \eta) x CO + (1 - \eta) \frac{y}{2} H_2 + \frac{d}{2} O_2 \\ & + jN_2 + a CO_2 + (3.76b - \frac{d}{2}) N_2 + dNO \end{aligned}$$

III. **Reaction type 3**: Incomplete combustion of "sweet gas" with oxides of nitrogen (NO_x) formation as both nitric oxide (NO) and nitrogen dioxide (NO₂) at combustion temperature, $T \ge 1600$ K.

$$\begin{split} & [\mathbf{C}_{x}\mathbf{H}_{y} + a\mathbf{CO}_{2} + j\mathbf{N}_{2}] + b(\mathbf{O}_{2} + 3.76\mathbf{N}_{2}) \rightarrow \\ & \eta x\mathbf{CO}_{2} + \eta \frac{v}{2}\mathbf{H}_{2}\mathbf{O} + (1 - \eta)x\mathbf{CO} + (1 - \eta)\frac{v}{2}\mathbf{H}_{2} + \frac{d}{4}\mathbf{O}_{2} \\ & + j\mathbf{N}_{2} + a\mathbf{CO}_{2} + (3.76b - \frac{d}{2})\mathbf{N}_{2} + \frac{d}{2}\mathbf{NO} + \frac{d}{2}\mathbf{NO}_{2} \end{split}$$

$$\end{split}$$
(5)

IV. Reaction type 4: Incomplete combustion of "sour gas" with no oxides of nitrogen (NO_x) formation at same condition as reaction type 1. H_2S assumed to be the only source of sulphur in the flared gas. '*m*' represents the available mole percentage of H_2S (Table 1).

$$[C_{x}H_{y} + aCO_{2} + jN_{2}] + b(O_{2} + 3.76N_{2}) + mH_{2}S \rightarrow \eta xCO_{2} + \eta \frac{v}{2}H_{2}O + (1 - \eta)xCO + [(1 - \eta)\frac{v}{2} + m]H_{2}$$
(6)
+(d - m)O_{2} + iN_{2} + aCO_{2} + 3.76bN_{2} + mSO_{2}

V. Reaction type 5: Incomplete combustion of "sour gas" with oxides of nitrogen (NO_x) formed as nitric oxide (NO) only at same condition as type 2.

$$\begin{split} & [\mathbf{C}_{x}\mathbf{H}_{y} + a\mathbf{CO}_{2} + j\mathbf{N}_{2}] + b(\mathbf{O}_{2} + 3.76\mathbf{N}_{2}) + m\mathbf{H}_{2}\mathbf{S} \rightarrow \\ & \eta x\mathbf{CO}_{2} + \eta \frac{y}{2}\mathbf{H}_{2}\mathbf{O} + (1 - \eta)x\mathbf{CO} + [(1 - \eta)\frac{y}{2} + m]\mathbf{H}_{2} \\ & + (\frac{d}{2} - m)\mathbf{O}_{2} + j\mathbf{N}_{2} + a\mathbf{CO}_{2} + (3.76b - \frac{d}{2})\mathbf{N}_{2} \\ & + d\mathbf{NO} + m\mathbf{SO}_{2} \end{split}$$
(7)

VI. **Reaction type 6**: Incomplete combustion of "sour gas" with oxides of nitrogen (NO_x) formation as both nitric oxide (NO) and Nitrogen dioxide (NO₂) oxides at same condition as type 3.

$$\begin{aligned} \left[C_{x}H_{y} + aCO_{2} + jN_{2} \right] + b(O_{2} + 3.76N_{2}) + mH_{2}S \rightarrow \\ \eta xCO_{2} + \eta \frac{y}{2}H_{2}O + (1 - \eta)xCO + [(1 - \eta)\frac{y}{2} + m]H_{2} \\ + (\frac{d}{4} - m)O_{2} + jN_{2} + aCO_{2} + (3.76b - \frac{d}{2})N_{2} \\ + \frac{d}{2}NO + \frac{d}{2}NO_{2} + mSO_{2} \end{aligned}$$
(8)

The total hydrocarbon (THC) of the gas from each field presented in Table 1 is computed using Eq. (9).

$$C_x H_y = \beta_1 C_1 H_1 + \beta_2 C_2 H_2 + \beta_3 C_3 H_3 + \dots + \beta_n C_i H_j \quad (9)$$

 C_i and H_j represent the individual hydrocarbon constituents that make up the THC in the associated natural gas. β_n is the molar/volume composition by percentage of C_i - H_j species from various fields. i = 1, 2, 3, 4, 5 and j = 4, 6, 8, 10, 12 for methane, ethane, propane, butane and pentane respectively. These reactions are computed in kilo moles and output (kg) computed using Eq. (11).

Emission
$$(kg) = Emission (kmol)$$

 \times Volume per kmol \times Molar mass (10)

Emission $(mmt) = Emission (kg) \times Annual gas flared (11)$

 Table 2
 Critical-point properties of some substance.

Substance	Temperature (K)	Pressure (Mpa)	Volume (m ³ /kmol)		
Air	132.5	3.77	0.0883		
Carbon dioxide	304.2	7.39	0.0943		
Carbon monoxide	133	3.5	0.093		
Hydrogen (normal)	33.3	1.3	0.0649		
Nitrogen	126.2	3.39	0.0899		
Nitrous oxide	309.7	7.27	0.0961		
Oxygen	154.8	5.08	0.078		
Sulphur dioxide	430.7	7.88	0.1217		
Water	647.1	22.06	0.056		

Eqs. (2)–(11) are coded in MATLAB and gas samples representing the average natural gas composition of various origins were run with various combinations of η nd δ to predict the gaseous emissions from gas flaring. The program was run with combination of $\delta = 1.3$, $\eta = 0.98$; $\delta = 0.98$, $\eta = 0.90$ and $\delta = 0.90$, $\eta = 0.74$ for each reaction type. The volumes used in equation 10 for all output emissions are the volume at critical point property (Table 2). The choice of critical thermodynamic behaviour of these emission gases at very high temperature at which gas flaring occur. To obtain annual estimate of emissions in million metric tonnes (mmt), the average output emission is multiplied by the annual gas flared for that year.

3. Results and discussion

Results predicted when operating conditions favouring incomplete combustion at various temperatures with or without NO_x formation are shown in Table 3 for sweet and sour natural gas flared. The tables show for each reaction type and field, the average emission output expected per unit gas flared. The average results were computed from results (tables not shown) of each combination of η nd δ or each reaction type.

The annual gas flaring emissions from annual gas flared in billion cubic metres (bcm) for CO₂, CO, NO, NO₂ and SO₂ are given in Tables 4. For validity, the predicted output for CO₂ is compared with annual world estimates as shown in Tables 4 and Fig. 1. The trend for this study shows that for an increasing gas flared volume, there is a consistent increase in the quantity of emission. This is however, not so for current world estimates. For example, between 2004 and 2008 where gas flaring in billion cubic metres increased from 112.3 to 141.3 bcm, this study shows a corresponding increase of CO₂ emissions from 456 million metric tonnes (mmt) to 573 mmt (Fig. 1). This is however, not so for estimates from the literature (GE, 2010; World Bank, 2012) which shows a decreasing trend for the same period. This is however possible if all flaring points had significant improvement on flare stack efficiency. While data for CO₂ emissions from gas flaring are readily available from the literature and environmental agencies worldwide, this is not so for other emissions from gas flaring. As at the time of this work, no data that show estimates of SO₂, NO, NO₂ and CO from gas flaring alone were encountered. However, results predicted here are a fraction of Global

Input				Output (kg)							
Sweet gas				R1–3	R1-3	R2	R3	R3			
Origin	Gas (THC)	CO ₂	H_2S	CO ₂	СО	NO	NO	NO ₂			
Soku	C _{1.0764} H _{4.1133}	0.002		3.91	0.36	0.94	0.47	0.72			
FS-2	C _{1.1375} H _{4.275}	0		3.23	0.29	0.98	0.49	0.75			
Groningen	C _{0.892} H _{3.48}	0.009		3.77	0.34	0.79	0.39	0.6			
Frigg	C _{1.029} H _{4.044}	0.003		3.96	0.36	0.91	0.45	0.7			
Hassi R'Mel	C _{1.088} H _{4.052}	0.002		4.44	0.4	0.93	0.47	0.71			
Urengoy	C _{1.222} H _{4.418}	0.004		2.71	0.25	1.03	0.51	0.79			
Kapumi	C _{0.743} H _{2.61}	0.438		6.32	0.41	0.62	0.31	0.47			
Maracalbo	C _{1.242} H _{4.45}	0.002		4.13	0.38	1.04	0.52	0.8			
AVERAGE				4.06	0.35	0.9	0.45	0.69			
Sour gas				R4–6	R4–6	R5	R 6	R6	R4–6		
				CO_2	CO	NO	NO	NO_2	SO_2		
Lacq	C _{0.822} H _{3.122}	0.09	0.153	3.35	0.27	0.71	0.36	0.55	1.2		
Uthmaniyah	C1.469H4.726	0.09	0.015	5.7	0.48	1.16	0.58	0.89	0.1		
Burgan	C _{1.322} H _{4.584}	0	0.001	4.79	0.44	1.09	0.54	0.83	0		
Kirkuk	C _{1.401} H _{4.59}	0.071	0.035	5.37	0.46	1.12	0.56	0.86	0.3		
AVERAGE				4.8	0.41	1.02	0.51	0.78	0.4		

Table 3Average emissions from natural gas.

Table 4 Annual emissions in MMT for NO, NO₂ and SO₂ from average values of all reaction conditions.

Year	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	Average
Flared gas (bcm)	112.6	101	107	111	112	135	135	136	141	147	138	140	126.3
Emission	Reactio	n types 1	-3 (sweet	gas)									
CO ₂	457	410	432	449	456	546	549	552	573	597	560	568	512
CO	39	35	37	38	39	47	47	47	49	51	48	49	44
NO (R-2)	102	91	97	100	101	122	122	123	128	133	125	126	114
NO (R-3)	51	46	48	50	51	61	61	61	64	66	62	63	57
NO ₂ (R-3)	78	70	74	77	78	94	94	94	98	102	96	97	87
	Reactio	n types 4	⊢6 (sour	gas)									
CO ₂	541	485	512	532	540	646	651	654	679	706	663	673	607
СО	47	42	44	46	46	56	56	56	58	61	57	58	52
SO ₂	45	40	42	44	45	53	54	54	56	58	55	56	50
NO (R-5)	115	103	109	113	114	137	137	138	144	150	141	143	129
NO (R-6)	57	51	54	57	57	69	69	69	72	75	70	71	64
NO ₂ (R-6)	88	79	84	87	87	105	105	106	110	115	108	109	99

Flared gas (bcm) Source: GE, 2010 and World Bank (2012).



Figure 1 A 5-year comparison of results for annual CO_2 emissions from gas flaring.

Estimates as presented in EDGAR version 4.2 (Fig. 2). For example, the CO predicted here from gas flaring is only about 5 percent of total global estimate from all sources. This trend is



Figure 2 Average Global Emissions (EC-JRC/PBL. EDGAR version 4.2. 2011) vs. Emissions from Gas flared (this work) between 2000 and 2008.

expected for all other emissions also. Hence, this work provides a means of comparison for other researches in gas flaring and other sources of pollution such as combustion from energy production and distribution, road transport, industrial processes etc.

4. Conclusion

This study has developed a model to predict and provide data for non-hydrocarbon emissions from gas flaring using mass balance equations. CO_2 , CO, NO, and NO_2 are the anticipated Non-hydrocarbon emissions from the flaring of sweet natural gas, while SO_2 is released in addition for sour gas flaring. These emissions degrade the environment and endanger human life, so knowing the type and quantity that this study predicts for any gas field or flow station is of paramount importance to all governments, environmental agencies and the oil and gas industry.

On the average, anticipated gaseous emissions from natural gas of global origins with an average annual global flaring rate of 126 bcm per year (between 2000 and 2011), CO₂ and CO emitted in million metric tonne (mmt) from flaring are 560 mmt and 48 mmt per annum. For NO, NO₂ and SO₂ the annual rate predicted by this model are 91 mmt, 93 mmt and 50 mmt per annum respectively. For, CO₂ this is within range to global estimates as reported by (Christopher et al., 2009; GE, 2010; World Bank, 2012). Few literature and estimates exist on other emissions and air pollutants from gas flaring. Focus has been on Green House Gas (Gas) like CO₂ and CH₄. Hence, this study provides such annual emission rate of CO, NO, NO₂ and SO₂ for future researches with the assumptions made in mind.

Given the challenges associated with gas flaring, its emissions, the impact on the environment and the difficulty in providing more accurate and single global estimates or data by various bodies concerned, care should be taken in selecting methods being employed. Inaccurate estimates or data of gas flared and the resulting emissions as sometimes reported, do not give the true impact of the operations of the oil and gas industry on the environment. Hence, more research and review of available methods (this model inclusive) is paramount to discouraging environmental degradation by this multibillion dollar industry.

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