



ORIGINAL ARTICLE

Modelling combustion reactions for gas flaring and its resulting emissions



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Abstract Flaring of associated petroleum gas is an age long environmental concern which remains unabated. Flaring of gas maybe a very efficient combustion process especially steam/air assisted flare and more economical than utilization in some oil fields. However, it has serious implications for the environment. This study considered different reaction types and operating conditions for gas flaring. Six combustion equations were generated using the mass balance concept with varying air and combustion efficiency. These equations were coded with a computer program using 12 natural gas samples of different chemical composition and origin to predict the pattern of emission species from gas flaring. The effect of key parameters on the emission output is also shown. CO₂, CO, NO, NO₂ and SO₂ are the anticipated non-hydrocarbon emissions of environmental concern. Results show that the quantity and pattern of these chemical species depended on percentage excess/deficiency of stoichiometric air, natural gas type, reaction type, carbon mass content, impurities, combustion efficiency of the flare system etc. These emissions degrade the environment and human life, so knowing the emission types, pattern and flaring conditions that this study predicts is of paramount importance to governments, environmental agencies and the oil and gas industry.

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1. Introduction

Despite the global campaign against the flaring of Associated Petroleum Gas (APG) during crude oil production and the resulting environmental degradation, gas flaring remains a major disposal option for unwanted APG. Flaring as a combus-

tion process is believed to burn efficiently. Nevertheless, if gas must be flared, an accurate means must be provided to determine the volume of gas flared and the quantity of the resulting emissions (Ismail and Umukoro, 2012). Combustion of fossil fuels such as APG in flares results in the emission of greenhouse gases (GHG) such as carbon dioxide (CO₂), methane (CH₄) and nitrous oxide which cause global warming (EPA, 2008). Also, depending on the waste gas composition and other factors, the emissions of pollutants from flaring may consist of unburned fuel (e.g. methane and volatile organic compounds) and byproducts of the combustion process (e.g. Soot, CO₂, CO, NO, NO₂, and SO₂) which are of health and environmental concern (Abdulkareem, 2005; EPA, 2011; Kahforoshan et al., 2008; Manshaa et al., 2010; Villasenor et al., 2003; Wilk and Magdziarz, 2010). CO causes reduction

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in oxygen-carrying capacity of the blood, which may lead to death. SO₂ also has an adverse effect on health, vegetation and buildings. Uncontrolled oxides of nitrogen emission could be injurious to health. When NO_x reacts with the oxygen in the air, the result is ground-level ozone which has very negative effects on the respiratory system and can cause inflammation of the airways, lung cancer etc. In the environmental context, NO_x contributes to acid deposition, lower air quality, visibility impairment, and eutrophication (EEA, 2012).

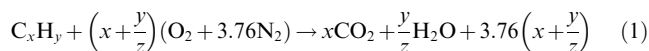
Quantifying flare emission has been very challenging. There is still high uncertainty in the measurement of flare emissions and combustion efficiencies because they are not measured directly from actual industrial flares. Hence, emission factors have been widely used in most studies to quantify emissions from hydrocarbon combustion. However, emission factors are not available for some emissions from flaring operations. The EPA for example, has no emission factor for flares and enclosed combustors for NO_x, CO, PM, SO₂ and some GHG (EPA, 2013). An attempt is made here to predict the quantity of chemical species from the flaring of associated natural gas using the mass balance concept with varying air and combustion efficiencies.

The quantity of these emissions generated from flaring is dependent on the combustion efficiency. The combustion efficiency generally expressed as a percentage is essentially the amount of Hydrocarbon (HC) converted to CO₂. It is the ratio between the mass of carbon in the form of carbon dioxide which is produced by the flare and the mass of carbon in the form of fuel entering the flare (Alberta Flare Research Project). In other words, the combustion efficiency of a flare as used here is a measure of how effective that flare is in converting all of the carbon in the fuel to CO₂. Properly operated flares achieve at least 98 percent combustion efficiency in the flare plume, meaning that hydrocarbon and CO emissions amount to less than 2% of species in the gas stream (EPA, 1995). Pohl et al. (1984), Pohl and Soelberg (1985) demonstrated that properly designed and operated industrial flares are highly efficient. Other studies indicated that flares have highly variable efficiencies, on the order of 62–99% (Stroscher 2000; Ozumba and Okoro, 2000; Leahey et al., 2001). In their experiments Becker (1974), Straitz (1977, 1978) cited in Goglek et al. (2010), observed a combustion efficiency of 75% during smoking conditions but 99% with steam assist to eliminate smoke. A flare operated within the envelope of stable operating conditions will exhibit high efficiency unless too much steam or air assist (excess air) is used. Excess air has implications on emissions, specifically related to the creation of NO_x. The availability of extra nitrogen found in the air and additional heat required to maintain combustion temperatures are favourable conditions for the formation of thermal NO (EPA, 2012). More so, greater amounts of excess air create lower amounts of CO but also cause more heat loss.

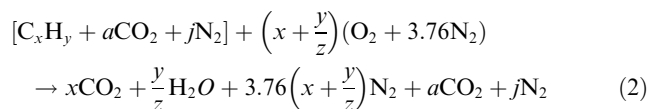
2. Methodology

Emission estimates from flaring gas in elevated flares are predicted here by generating mass balance equations for various flaring conditions. This model depends largely on the number that precedes the formula for chemical species involved in the chemical reactions and is termed the stoichiometric coefficient. Mass balance in combustion analysis is central to determining flare combustion efficiency (Prateep et al., 2012; Johnson,

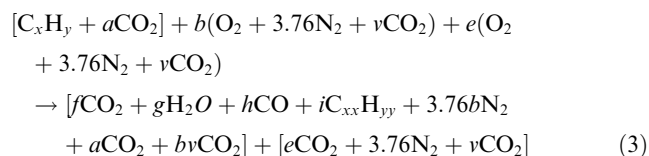
2008) and hence, flares emissions. Sonibare and Akeredolu (2004) investigated seven possible reactions (conditions) for flaring of natural gas using mass balance equations. Six of these were conditions that favour incomplete combustion. The general equation for complete combustion of pure alkanes (hydrocarbon) which are known to be the major constituent of natural gas is given by:



For natural gas, very little systematic information is available concerning its chemical composition. Based on the chemical composition (Table 1), Eq. (2) can be written for the complete combustion of sweet natural gas.

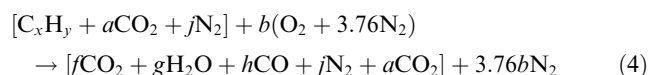


where C_xH_y represent the known composition of total hydrocarbon (THC) of the flared gas. 'z' is equal to 4 for complete combustion, while 'a' and 'j' are the stoichiometric coefficients of the N₂ and CO₂ in the flared gas stream as shown in Table 1. Flaring in reality is rarely successful in the achievement of complete combustion (Leahey et al., 2001). Kostiuk et al. (2004) considered this by showing overall stoichiometry in estimating combustion efficiency as seen from a point downstream of the flare in Eq. (3). Hence, flaring is considered as an incomplete combustion process.

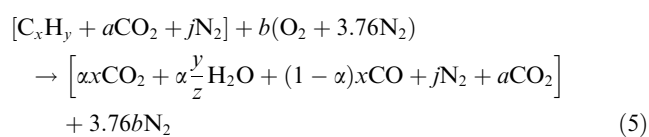


where, 'b' and 'e' are stoichiometric coefficients for air in combustion and for air entrained into the plume without combustion, respectively. Considering the chemical composition (Table 1) and the following assumptions, Eq. (3) can be rewritten for sweet natural gas (no presence of sulphur):

- i. 'i' = 0, (no unburned hydrocarbon),
- ii. 'v' is very small in the composition of air when compared to nitrogen and oxygen,
- iii. 'e' = 0 (No ambient air entrained into the plume without combustion).



The distribution of chemical specie on the product side of Eq. (4) is also a function of the molar fraction between the fully oxidized carbon and the partial oxidized carbon (Kostiuk et al., 2004). After algebraic manipulation and equation balancing, Eq. (4) can be re-written as:



From Eqs. 1, 4, and 5, $b = \left(x + \frac{y}{z}\right)$, $f = \alpha x$, $g = \alpha \frac{y}{z}$, ($h = 1 - \alpha$)x and α is the molar fraction between oxidized

Table 1 Natural gas composition in percentage moles/volume employed in the study.

Gas fields	Chemical compound					N ₂	CO ₂	H ₂ S	Gas field	Origin
	Methane	Ethane	Propane	Butane	Pentane +					
1	92.506	2.7801	1.6582	0.7791	0.2971	0.1141	0.2182	–	Soku	(NIG)
2	81.3	2.9	0.4	0.1	0.1	14.3	0.9	–	Groningen	(NLD)
3	69	3	0.9	0.5	0.5	1.5	9.3	15.3	Lacq	(FRA)
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	(DZA)
6	85.3	5.8	5.3	2.1	0.2	0.9	0.4	–	Urengoy	(CIS)
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	55.5	18	9.8	4.5	1.6	0.2	8.9	1.5	Uthmaniyah	(SAU)
10	74.3	14	5.8	2	0.9	2.9	–	0.1	Burgan	(KWT)
11	56.9	21.2	6	3.7	1.6	–	7.1	3.5	Kirkuk	(IRQ)
12	90.12	6.94	2.09	0.771	0.079	–	–	–	S-2	(NIG)

Source: a-1, b-2–11, c-4.

a-1: Natural gas composition data of field (1) obtained from Shell Petroleum Development company's flow station in Soku, Rivers State, Nigeria.

b-2–11: Natural gas composition data of field (2–11) from Vailais (1983) cited in Rojey et al. (1997).

c-4: Natural gas composition data of field (12) from Sonibare and Akeredolu (2004).

Carbon (CO₂), and partial oxidized Carbon (CO). The stoichiometric coefficient 'b' (i.e. Normal, excess or deficiency of combustion air) and CE of the flare have visible effects on the product side of the reaction. This is clearly shown by varying the combustion efficiency (η), air (b) and natural gas type in the equations generated. The combustion efficiency (mass based) expressed in terms of the stoichiometric coefficient (Kostiuk et al., 2004) in Eq. (5) is given by:

$$\eta = \frac{f}{f+h} \quad (6)$$

Substituting for $f = \alpha x$ and $h = (1 - \alpha)x$ gives;

$$\eta = \alpha \quad (7)$$

In this study, 6 equations for incomplete combustion of natural gas are presented with varying efficiencies and air available for combustion. The value of 'z', is computed for a given percentage excess or deficiency (δ) of combustion air using Eqs. (8)–(10).

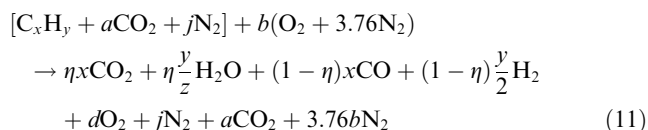
$$\delta = \frac{b}{k'} \quad (8)$$

$$k = \left(x + \frac{y}{4}\right) \quad (9)$$

$$b = \left(x + \frac{y}{z}\right) \quad (10)$$

where 'k' is the theoretical air for complete combustion ($k = b$ at $z = 4$) and 'b' is the actual air that took part in the combustion process.

I. Reaction type 1: Incomplete combustion of "sweet gas" without the formation of oxides of nitrogen (NO_x).



$$\text{where } d = \left[x \left(\frac{1}{2} - \frac{\eta}{2} \right) + y \left(\frac{1}{Z} - \frac{\eta}{2} \right) \right] \quad (12)$$

'a' is the known stoichiometric coefficient for CO₂ in flare stream (Table 1)

'b' is the unknown stoichiometric coefficient for the air involved in combustion

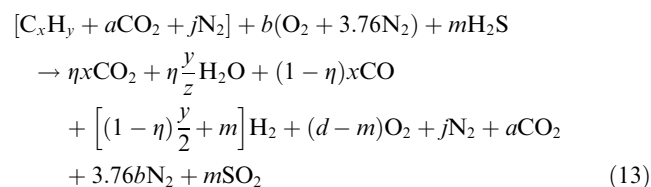
'j' is the known stoichiometric coefficient for N₂ in flare stream (Table 1)

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

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

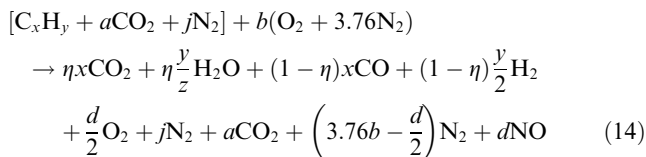
For this reaction type, it is assumed that the existing temperature in the combustion zone is assumed to be less than 1200 Kelvin (K) as oxides of nitrogen start formation at this temperature (Selcuk, 2000 cited in Sonibare and Akeredolu (2004), Leahey et al., 2001). Soot and volatile organic compounds (VOC) are negligible here and in subsequent reactions, because of the natural gas low propensity to soot (Kostiuk et al., 2004) and Gogolek et al. (2010) showed no VOC were found in the combustion of natural gas itself.

II. Reaction type 2: Incomplete combustion of "sour gas" with no oxides of nitrogen (NO_x) formation.



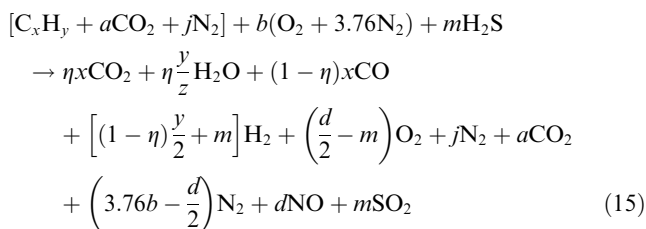
Reaction conditions are same as reaction type 1 above with H₂S assumed to be the only source of sulphur in the flared gas. 'm' represents the available mole percentage of H₂S (Table 1).

III. **Reaction type 3:** Incomplete combustion of “sweet gas” with oxides of nitrogen (NO_x) formed as nitric oxide (NO) only.



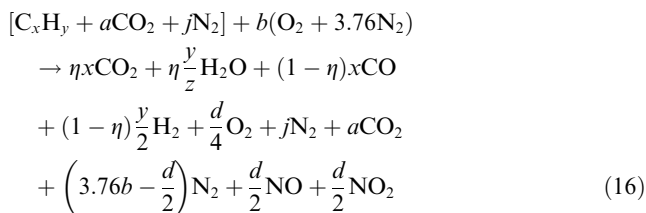
Reaction temperature (T) in kelvin is assumed to be $1200 \text{ K} \leq T \leq 1600 \text{ K}$. Some percentage of the nitrogen present in air is assumed to be converted to nitric oxide while the remaining is released as free nitrogen (N_2).

IV. **Reaction type 4:** Incomplete combustion of “sour gas” with oxides of nitrogen (NO_x) formed as nitric oxide (NO) only.



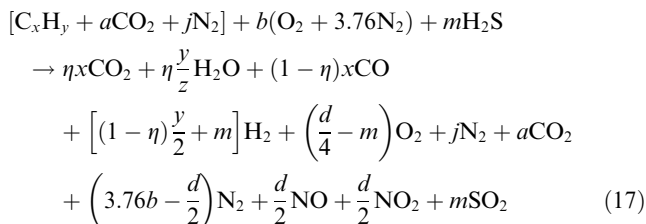
Existing condition in reaction type 3 in “sweet gas” combustion is assumed but with addition of SO_2 in emission output as a result of H_2S present in the composition of natural gas.

V. **Reaction type 5:** Incomplete combustion of “sweet gas” with oxides of nitrogen (NO_x) formation as both nitric oxide (NO) and nitrogen dioxide (NO_2).



The rate of reaction that forms thermal NO_x is highly dependent upon peak flame temperature and the stoichiometric ratio in the primary combustion zone (Biarnes et al., 2009). Assumption here is that the combustion temperature, $T \geq 1600 \text{ K}$. Nitrogen present is converted to both nitric oxide and nitrogen dioxide at the high temperatures of the flame core with some released as free nitrogen.

VI. **Reaction type 6:** Incomplete combustion of “sour gas” with oxides of nitrogen (NO_x) formation as both nitric oxide (NO) and nitrogen dioxide (NO_2) oxides.



Existing condition in reaction type (5) in “sweet gas” combustion is assumed.

The total hydrocarbon (THC) of the APG from each field presented in Table 1 is computed using formula for combustion of multicomponent fuel (McAllister et al., 2011) as expressed in Eq. 18 and 19. These equations are coded in MATLAB and gas samples representing the average natural gas composition of various origins were run with it to predict the gaseous emissions from gas flaring and to model the effect of various flaring conditions and parameters.

$$\text{C}_x = \beta_1\text{C}_1 + \beta_2\text{C}_2 + \beta_3\text{C}_3 + \dots + \beta_n\text{C}_i \quad (18)$$

$$\text{H}_y = \beta_1\text{H}_1 + \beta_2\text{H}_2 + \beta_3\text{H}_3 + \dots + \beta_n\text{H}_j \quad (19)$$

$$\text{Air-Fuel Ratio} = \frac{(x + y/z)(4.76 * 29)}{12x + y} \quad (20)$$

C_i and H_j represent the individual HC constituents that make up the THC in the APG. β_n is the molar/volume composition by percentage of C_iH_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.

3. Results and discussion

Results for operating conditions which favour complete and incomplete combustion are presented in Tables 2–6 for sweet natural gas. The results give the output emissions of combustion products in Kilograms for a unit natural gas flared at different percentage excess or deficiency of air used (δ) and efficiency of flare system (η). This is obtained by multiplying the initial output of all gaseous flaring emissions by the molar mass of each output. For all results presented, only harmful and concerned gaseous emissions are shown. The CO_2 emission output is a combination of CO_2 from the combustion of THC in the natural gas and the CO_2 originally present in the composition of the gas flared. Other emission outputs such as the O_2 , H_2O , N_2 , and H_2 have not been shown in result tables for ease of presentation.

Emissions from sweet natural gas flared for condition that favours reaction types 1, 3 and 5 are presented in Tables 2–5 with groupings done according to air used (δ) and efficiency (η). Tables 2–4 show simulation results for $\delta = 1.3$ ($\eta = 0.98, 0.74, 0.5$), $\delta = 0.98$ ($\eta = 0.90, 0.74, 0.5$) and $\delta = 0.90$ ($\eta = 0.85, 0.74, 0.5$) respectively. Substituting $\delta = 100\%$ and $\eta = 100\%$ into the incomplete combustion reactions for this model gives the result for complete combustion with no other emissions other than CO_2 , H_2O and N_2 as shown in Table 6. This, validates this model, as complete combustion of hydrocarbon (C_xH_y) yields only the aforementioned products (Weston, 1992; McAllister et al., 2011). In addition, the Air–Fuel (A/F) ratios determined by Eq. (20) for this work have close values to that in literatures. The difference (due to approximations in mass of air used) in values is between 0.3% and 0.5% for output of methane and other similar gas profile compared in Table 6.

Similarly, results for sour natural gas which produces SO_2 in addition to the emissions presented for sweet natural gas are shown in Tables 7–9 for flaring condition that favours reaction types 2, 4 and 6. Results are for efficiencies of $\delta = 1.3$ ($\eta = 0.98, 0.74$ and 0.50), $\delta = 0.98$ ($\eta = 0.90, 0.74$

Table 2 Non HC-emissions from sweet natural gas, for 130% air and efficiency of 98%, 74% and 50%, respectively.

Origin	Inputs			Outputs (kg)															
				$\delta = 1.3; \eta = 0.98$					$\delta = 1.3; \eta = 0.74$					$\delta = 1.3; \eta = 0.50$					
	Reaction types			1,3,5	1,3,5	R3	R5	R5	1,3,5	1,3,5	R3	R5	R5	1,3,5	1,3,5	R3	R5	R5	
Natural gas			CO ₂	Air	CO ₂	CO	NO	NO	NO ₂	CO ₂	CO	NO	NO	NO ₂	CO ₂	CO	NO	NO	NO ₂
Soku	C _{1.076} H _{4.11}	0.002	2.74	46.53	0.6	29.16	14.58	19.88	35.16	7.84	45.70	22.85	31.16	23.79	15.07	62.25	31.12	42.44	
Groningen	C _{0.892} H _{3.48}	0.009	2.29	38.87	0.5	24.42	12.21	16.65	29.45	6.49	38.31	19.16	26.12	20.03	12.49	52.21	26.11	35.6	
Frigg	C _{1.029} H _{4.044}	0.003	2.65	44.51	0.58	28.27	14.14	19.28	33.64	7.49	44.38	22.19	30.26	22.77	14.41	60.49	30.24	41.24	
Hassi R'Mel	C _{1.088} H _{4.052}	0.002	2.73	47.02	0.61	29.1	14.55	19.84	35.52	7.92	45.55	22.77	31.05	24.03	15.23	61.99	30.99	42.26	
Urengoy	C _{1.222} H _{4.418}	0.004	3.02	52.88	0.68	32.22	16.11	21.97	39.98	8.9	50.34	25.17	34.32	27.07	17.11	68.45	34.23	46.67	
Kapumi	C _{0.743} H _{2.61}	0.438	1.81	51.33	0.42	19.32	9.66	13.17	43.48	5.41	30.14	15.07	20.55	35.63	10.4	40.95	20.47	27.92	
Maracalbo	C _{1.242} H _{4.45}	0.002	3.06	53.66	0.7	32.6	16.3	22.23	40.54	9.04	50.91	25.46	34.71	27.42	17.39	69.22	34.61	47.19	
S-2	C _{1.1375} H _{4.275}	0.000	2.87	49.06	0.64	30.56	15.28	20.84	37.05	8.28	47.86	23.93	32.63	25.03	15.92	65.15	32.57	44.42	
	Average			47.98	0.59	28.21	14.10	19.23	36.85	7.67	44.15	22.08	30.10	25.72	14.75	60.09	30.04	40.97	

Table 3 Non HC-emissions from sweet natural gas, for 98% air and efficiency of 90%, 74% and 50%, respectively.

Origin	Inputs			Outputs (kg)															
				$\delta = 0.98; \eta = 0.90$					$\delta = 0.98; \eta = 0.74$					$\delta = 0.98; \eta = 0.50$					
	Reaction types			1,3,5	1,3,5	R3	R5	R5	1,3,5	1,3,5	R3	R5	R5	1,3,5	1,3,5	R3	R5	R5	
Natural gas			CO ₂	Air	CO ₂	CO	NO	NO	NO ₂	CO ₂	CO	NO	NO	NO ₂	CO ₂	CO	NO	NO	NO ₂
Soku	C _{1.076} H _{4.11}	0.002	2.06	42.74	3.01	5.04	2.52	3.44	35.16	7.84	16.07	8.03	10.96	23.79	15.07	32.61	16.31	22.24	
Groningen	C _{0.892} H _{3.48}	0.009	1.73	35.73	2.5	4.24	2.12	2.89	29.45	6.49	13.5	6.75	9.21	20.03	12.49	27.4	13.7	18.68	
Frigg	C _{1.029} H _{4.044}	0.003	2	40.89	2.88	4.92	2.46	3.35	33.64	7.49	15.66	7.83	10.67	22.77	14.41	31.77	15.88	21.66	
Hassi R'Mel	C _{1.088} H _{4.052}	0.002	2.06	43.18	3.05	5	2.5	3.41	35.52	7.92	15.96	7.98	10.88	24.03	15.23	32.41	16.2	22.09	
Urengoy	C _{1.222} H _{4.418}	0.004	2.28	48.58	3.42	5.5	2.75	3.75	39.98	8.9	17.58	8.79	11.99	27.07	17.11	35.69	17.85	24.34	
Kapumi	C _{0.743} H _{2.61}	0.438	1.37	48.71	2.08	3.28	1.64	2.23	43.48	5.41	10.49	5.24	7.15	35.63	10.4	21.3	10.65	14.52	
Maracalbo	C _{1.242} H _{4.45}	0.002	2.31	49.28	3.48	5.56	2.78	3.79	40.54	9.04	17.76	8.88	12.11	27.42	17.39	36.07	18.03	24.59	
S-2	C _{1.1375} H _{4.275}	0.000	2.16	45.05	3.18	5.26	2.63	3.59	37.05	8.28	16.79	8.4	11.45	25.03	15.92	34.08	17.04	23.24	
	Average			44.27	2.95	4.85	2.425	3.306	36.85	7.6713	15.47625	7.7375	10.553	25.72	14.753	31.416	15.708	21.42	

Table 4 Non HC-emissions from sweet natural gas, for 90% air and efficiency of 85, 74 and 50% respectively.

Origin	Inputs		Outputs (kg)																
			$\delta = 0.90; \eta = 0.85$				$\delta = 0.90; \eta = 0.74$				$\delta = 0.90; \eta = 0.50$								
			1,3,5	CO ₂	CO	Air	R3	NO	R5	NO ₂	R5	NO	R5	NO ₂	R3	NO	R5	NO	R5
Natural gas	CO ₂	Air																	
Soku	C _{1,076} H _{4,11}	0.002	1.89	40.37	4.52	1.08	0.54	0.74	7.84	8.66	4.33	5.9	23.79	15.07	25.2	12.6	17.18		
Groningen	C _{0,892} H _{3,48}	0.009	1.59	33.77	3.75	0.93	0.47	0.64	29.45	7.3	3.65	4.98	20.03	12.49	21.2	10.6	14.45		
Frigg	C _{1,029} H _{4,044}	0.003	1.84	38.62	4.32	1.09	0.55	0.74	33.64	8.48	4.24	5.78	22.77	14.41	24.59	12.29	16.76		
Hassi R'Mel	C _{1,088} H _{4,052}	0.002	1.89	40.79	4.57	1.03	0.52	0.7	35.52	8.57	4.28	5.84	24.03	15.23	25.01	12.5	17.05		
Urengoy	C _{1,222} H _{4,418}	0.004	2.09	45.89	5.13	1.09	0.54	0.74	39.98	9.39	4.69	6.4	27.07	17.11	27.5	13.75	18.75		
Kapami	C _{0,743} H _{2,61}	0.438	1.26	47.07	3.12	0.62	0.31	0.42	43.48	5.41	2.79	3.8	35.63	10.4	16.39	8.19	11.17		
Maracalbo	C _{1,242} H _{4,45}	0.002	2.12	46.55	5.22	1.08	0.54	0.74	40.54	9.47	4.74	6.46	27.42	17.39	27.78	13.89	18.94		
S-2	C _{1,1375} H _{4,275}	0.000	1.99	42.55	4.78	1.1	0.55	0.75	37.05	8.28	4.51	6.15	25.03	15.92	26.32	13.16	17.94		
Average			41.95	4.4263	1.0025	0.5025	0.684	36.85	7.6713	8.30875	4.1538	5.6638	25.72	14.753	24.249	12.123	16.53		

and 0.50), $\delta = 0.90$ ($\eta = 0.74$ and 0.50), and $\delta = 0.76$ ($\eta = 0.50$) for each reaction type. The presence of H₂S in reaction types 2, 4 and 6 indicates the difficulty in attaining complete combustion. This is because such reaction requires excess air for SO₂ formation and to ensure the combustion of H₂S in the natural gas. This also shows that impurities in the composition of flared natural gas hinder complete combustion.

For reaction type 1, CO comes as an additional product for incomplete combustion, though with a reduction in CO₂. The additional O₂ released poses no problem to the environment since the reaction does not favour conversion of nitrogen to NO. This is however, not so for reactions type 3 and 5 (Fig. 1) which favour the formation of NO and NO₂ at temperature above 1200 K but below 1600 K. For this model, the formation of NO₂ in reaction type 5 leads to 50% reduction in the formation of NO.

Reaction types 2, 4 and 6 (Fig. 2) modelled for sour gas flaring are similar to reaction types 1, 3 and 5 previously discussed but with the addition of SO₂ formation resulting from the presence of H₂S in the natural gas. For the formation of SO₂, oxygen molecules are required; hence, the more excess air available, the more SO₂ will be formed.

The average values from the simulation of molar/volume composition of 12 gas fields for 6 reaction types, show that reaction type influences the NO, NO₂ and SO₂ but not CO₂ and CO. Hence, the option for determining operating conditions for gas flare sites should be based on which NO or NO₂ poses more threat to the environment or human life. However, reaction type 1 for sweet natural gas and reaction type 2 for sour natural gas offer the best operating condition if natural gas is to be flared. This is because these reaction types do not favour formation of Nitrous oxides in addition to CO₂ and CO.

3.1. Effect of combustion efficiency (η) and excess or deficiency air (δ) on flaring emissions

The percentage excess or deficiency in air is a very important factor, if not the most important, which determines whether flaring favours complete or incomplete combustion. Results (Fig. 3) show that for the same reaction type (reaction 5 for example), CO₂, CO, NO and NO₂ change with the changing values of ' δ '. CO₂, NO, and NO₂ decrease with decreasing δ (from 1.3 to 0.76) for a unit hydrocarbon gas flared. However, this is not so for CO which increases with decreasing air for combustion. The implication for this is that, air assisted flare or other system which may encourage combustion of natural gas in excess of stoichiometric air will have an increase in CO₂, NO and NO₂ emissions. This is in agreement with World Bank (1999) that low excess air firing has the benefit of reducing NO_x and with Kostiuk et al. (2004) that over steaming or excess air at low waste gas flow should be avoided. Hence, the choice of operating condition for flare system also depends on the comparative impact of CO set against other emissions like CO₂, NO and NO₂ on our environment and human life.

Combustion Efficiency is influenced greatly by temperature, wind velocity, turbulence in reaction domain etc. Some of these factors were taken care of by the introduction of CE (η) to the mass balance equations. For example, in reaction types 1 and 6 (Figs. 4 and 5), the outputs for four gas field flare

Table 5 Emissions from sweet gas, for $\delta = 76\%$ and $\eta = 50\%$.

Origin	Inputs			Outputs (kg)				
	Reaction types			$\delta = 0.76; \eta = 0.50$				
	Natural gas	CO ₂	Air	CO ₂	CO	NO	NO	NO ₂
Soku	C _{1.076} H _{4.11}	0.002	1.6	23.79	15.07	12.24	6.12	8.34
Groningen	C _{0.892} H _{3.48}	0.009	1.34	20.03	12.49	10.35	5.17	7.05
Frigg	C _{1.029} H _{4.044}	0.003	1.55	22.77	14.41	12.02	6.01	8.19
Hassi R'Mel	C _{1.088} H _{4.052}	0.002	1.6	24.03	15.23	12.07	6.03	8.23
Urengoy	C _{1.222} H _{4.418}	0.004	1.77	27.07	17.11	13.17	6.59	8.98
Kapumi	C _{0.743} H _{2.61}	0.438	1.06	35.63	10.4	7.79	3.9	5.31
Maracalbo	C _{1.242} H _{4.45}	0.002	1.79	27.42	17.39	13.27	6.64	9.05
S-2	C _{1.1375} H _{4.275}	0.000	1.68	25.03	15.92	12.73	6.36	8.68
	Average			25.72	14.753	11.705	5.8525	7.979

Table 6 Non HC emission and Air–Fuel (A/F) ratio from complete combustion.

Origin	Inputs			Outputs (kg)				This work	Weston 2011	Sonibare 2004
	Reaction type			$\delta = 1; \eta = 1$						
	Natural gas	CO ₂	Air	Complete combustion						
				CO ₂	H ₂ O	CO	N ₂	A/F	A/F	A/F
Methane	CH ₄	0	2	44.01	36	0	210.56	17.25	17.16	17.167
Soku	C _{1.07643} H _{4.1133}	0.002	2.1	47.47	37.05	0	221.69	17.06	–	–
Groningen	C _{0.892} H _{3.48}	0.009	1.76	39.66	31.35	0	185.59	17.15	–	–
Frigg	C _{1.029} H _{4.044}	0.003	2.04	45.42	36.43	0	214.87	17.18	–	–
Hassi R'Mel	C _{1.088} H _{4.052}	0.002	2.1	47.97	36.5	0	221.3	16.95	–	–
Urengoy	C _{1.222} H _{4.418}	0.004	2.33	53.96	39.8	0	245.05	16.83	–	–
Kapumi	C _{0.743} H _{2.61}	0.438	1.4	51.98	23.51	0	146.99	16.71	–	–
Maracalbo	C _{1.242} H _{4.45}	0.002	2.35	54.75	40.08	0	248	16.79	–	–
S-2	C _{1.1375} H _{4.2749}	0.000	2.21	50.06	38.51	0	232.38	16.99	–	16.904
	Average			48.91	35.404	0	214.48	16.9575	–	–

emissions are shown for $\delta = 98\%$ ($\eta = 90\%$, 74%) i.e. δ being constant. For each of the gas field considered, CO₂ will decrease with decreasing η while CO, NO and NO₂ increase by more than 50%. The SO₂ output remains the same for this model. A similar pattern is obtainable for other gas fields in all reaction types considered. The implication for this is that, more CO₂ will be generated if efficiency as used here, favours reduction in CO, NO and NO₂ (e.g. Increasing ' η ' from 0.74 to 0.9). The range is about 17–34% increase in CO₂ output and between 90% and 105% decrease in CO, NO and NO₂ emissions, and vice versa for all reaction types. Hence, keeping the reaction condition for flaring at $\delta \geq 90\%$ and ' η ' far greater than 50% should be the norm if natural gas is to be flared, especially in regions where either the means for effective utilization of this gas is not available or where flaring becomes more economical than utilization of this natural gas, as sometimes is.

3.2. Effect of assuming 100% methane (CH₄) for composition of gas flared

Methane which is the lightest known hydrocarbon is the major constituent of natural gas. Hence, experiments, analysis, simulations and various models are mostly based on the behaviour

of methane. This is not the case in this study. Natural gas is considered by calculating the total carbon and hydrogen which make up the total hydrocarbon of the gas being flared. The CO₂ in the chemical composition of the flared gas is also accounted for in this model. A comparison of natural gas flaring emission for this study and that using only methane is shown in Fig. 6 for Soku and Groningen. The assumption of methane only gives between 7% and 35% error in the actual emissions from gas flaring for all fields considered. More so, the same emission is obtained for all oil fields (with methane only), regardless of the variation in the molar/volumetric composition of natural gas from each field. This may be too large an error to neglect for certain analysis. Also, fields with more carbon mass content (heavy or light HC) produced more CO₂ and CO.

4. Conclusion

This study has developed a model based on the possible individual combustion types, to predict chemical species in gas flaring emission and the effect of some key factors that influence gas flaring as a combustion process. Six different combustion reaction equations for incomplete combustion (flaring process) were coded using MATLAB program. CO₂, CO,

Table 7 Non HC-Emissions from sour natural gas, for 130% air and efficiency of 98, 74 and 50% respectively. .

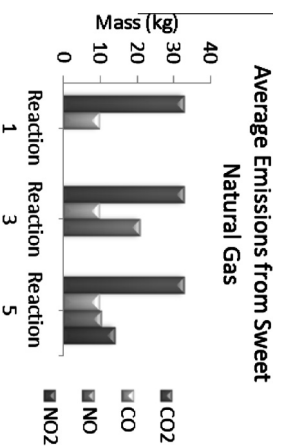
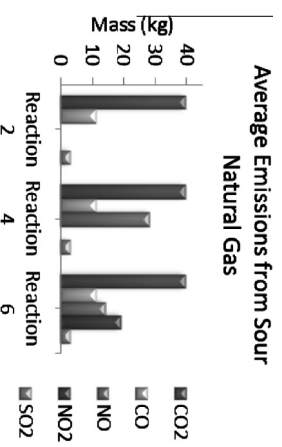
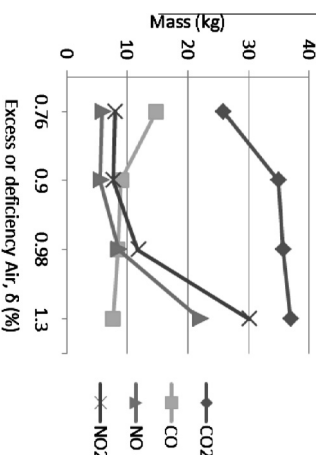
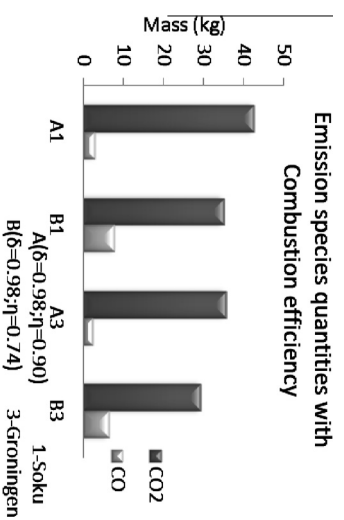
Origin	Inputs				Outputs (kg)															For all η and R SO ₂
	Reaction types				$\delta = 1.3; \eta = 0.98$					$\delta = 1.3; \eta = 0.74$					$\delta = 1.3; \eta = 0.50$					
	Natural gas	CO ₂	H ₂ S	Air	2,4,6 CO ₂	2,4,6 CO	R4 NO	R6 NO	R6 NO ₂	2,4,6 CO ₂	2,4,6 CO	R4 NO	R6 NO	R6 NO ₂	2,4,6 CO ₂	2,4,6 CO	R4 NO	R6 NO	R6 NO ₂	
Lacq	C _{0.822} H _{3.122}	0.093	0.153	2.08	39.54	0.46	22.2	11.1	15.14	30.86	5.98	34.78	17.39	23.72	22.18	11.51	47.37	23.68	32.3	9.8
Uthmaniyah	C _{1.469} H _{4.726}	0.089	0.015	3.45	67.28	0.82	36.67	18.34	25	51.76	10.69	56.91	28.45	38.8	36.25	20.57	77.14	38.57	52.59	0.96
Burgan	C _{1.322} H _{4.584}	0	0.001	3.21	57.02	0.74	34.17	17.08	23.3	43.05	9.62	53.25	26.62	36.31	29.09	18.51	72.33	36.17	49.32	0.06
Kirkuk	C _{1.401} H _{4.59}	0.071	0.035	3.31	63.54	0.78	35.27	17.63	24.05	48.75	10.2	54.78	27.39	37.35	33.95	19.61	74.3	37.15	50.66	2.24
	Average				56.85	0.7	32.0775	16.04	21.873	43.61	9.1225	49.93	24.963	34.045	30.37	17.55	67.785	33.8925	46.2175	3.265

Table 8 Non HC-Emissions from sour natural gas, for 98% air and efficiency of 90%, 74% and 50%, respectively.

Origin	Inputs				Outputs (kg)															For all η and R SO ₂
	Reaction types				$\delta = 0.98; \eta = 0.90$					$\delta = 0.98; \eta = 0.74$					$\delta = 0.98; \eta = 0.50$					
	Natural gas	CO ₂	H ₂ S	Air	2,4,6 CO ₂	2,4,6 CO	R4 NO	R6 NO	R6 NO ₂	2,4,6 CO ₂	2,4,6 CO	R4 NO	R6 NO	R6 NO ₂	2,4,6 CO ₂	2,4,6 CO	R4 NO	R6 NO	R6 NO ₂	
Lacq	C _{0.822} H _{3.122}	0.093	0.153	1.57	32.56	2.3	3.83	1.92	2.61	30.86	5.98	12.22	6.11	8.33	22.18	11.51	24.8	12.4	16.91	9.8
Uthmaniyah	C _{1.469} H _{4.726}	0.089	0.015	2.60	58.19	4.11	6.1	3.05	4.16	51.76	10.69	19.59	9.79	13.35	36.25	20.57	39.82	19.91	27.15	0.96
Burgan	C _{1.322} H _{4.584}	0	0.001	2.42	52.36	3.7	5.78	2.89	3.94	43.05	9.62	18.5	9.25	12.61	29.09	18.51	37.58	18.79	25.62	0.06
Kirkuk	C _{1.401} H _{4.59}	0.071	0.035	2.50	55.49	3.92	5.89	2.94	4.01	48.75	10.2	18.9	9.45	12.89	33.95	19.61	38.41	19.21	26.19	2.24
	Average				49.65	3.5075	5.4	2.7	3.68	43.61	9.1225	17.303	8.65	11.795	30.37	17.55	35.153	17.5775	23.9675	3.265

Table 9 Non HC-Emissions from sour natural gas, for 90% and 76% air and efficiency of 74% and 50%, respectively.

Origin	Inputs				Outputs (kg)										Input Air	Outputs (kg)				
	Reaction types				$\delta = 0.9; \eta = 0.74$					$\delta = 0.90; \eta = 0.5$						$\delta = 0.76; \eta = 0.50$				
					2,4,6	2,4,6	R4	R6	R6	2,4,6	2,4,6	R4	R6	R6		2,4,6	2,4,6	R4	R6	R6
	Natural gas	CO ₂	H ₂ S	Air	CO ₂	CO	NO	NO	NO ₂	CO ₂	CO	NO	NO	NO ₂		CO ₂	CO	NO	NO	NO ₂
Lacq	C _{0.822} H _{3.122}	0.093	0.153	1.44	30.86	5.98	6.58	3.29	4.49	22.18	11.51	19.16	9.58	13.07	1.22	22.18	11.51	9.29	4.65	6.33
Uthmaniyah	C _{1.469} H _{4.726}	0.089	0.015	2.39	51.76	10.69	10.26	5.13	6.99	36.25	20.57	30.49	15.24	20.79	2.01	36.25	20.57	14.16	7.08	9.66
Burgan	C _{1.322} H _{4.584}	0	0.001	2.22	43.05	9.62	9.81	4.91	6.69	29.09	18.51	28.89	14.45	19.7	1.88	29.09	18.51	13.69	6.85	9.34
Kirkuk	C _{1.401} H _{4.59}	0.071	0.035	2.29	48.75	10.2	9.93	4.96	6.77	33.95	19.61	29.44	14.72	20.07	1.94	33.95	19.61	13.74	6.87	9.37
Average					43.61	9.1225	9.145	4.573	6.235	30.37	17.55	26.995	13.498	18.4075		30.37	17.55	12.72	6.3625	8.675

**Figure 1** Emissions from Reaction types 1, 3 and 5.**Figure 2** Emissions from Reaction types 2, 4 and 6.**Figure 3** Emissions with excess/deficiency of air (δ).**Figure 4** Emissions with efficiency (η) for 2 gas fields, Reaction type 1.

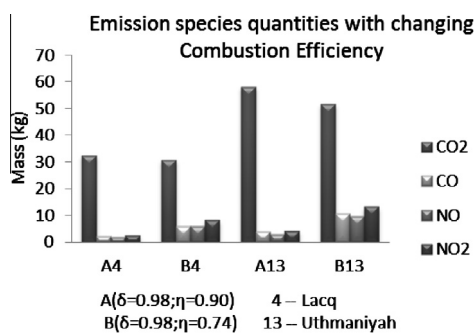


Figure 5 Emissions with efficiency (η) for 2 gas fields.

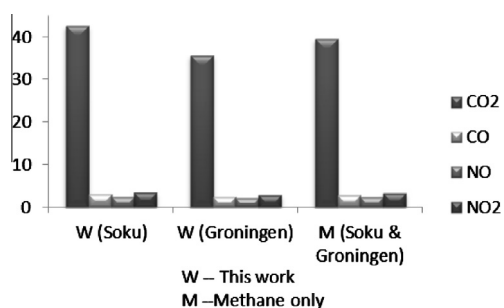


Figure 6 Comparison between this study and modelling with CH₄ only for 2 fields.

NO, NO₂ and SO₂ are the anticipated Non-HC gaseous emissions of environmental concern from the flaring of associated natural gas. Going by product pattern of sweet natural gas for reaction type 1, CO₂ and CO emitted from flaring are 35.01 kg and 8.84 kg, respectively, per unit of flared gas. The same trend is seen in reaction types 3 and 5 but with the addition of 23.24 kg NO in reaction type 3, and 12.12 kg and 16.52 kg of NO and NO₂ for reaction type 5. A similar trend is also observed in reaction types 2, 4 and 6 but with an increase in CO₂ and CO of 39.87 kg and 11.31 kg. Also, there is an increase in NO and NO₂ emission for reaction types 4 and 6 and a predicted SO₂ of 3.625 kg.

The likely reaction types shown in this study and the operating conditions under which they occur indicate that operators of natural gas flares need to be watchful at the conditions allowed for flaring. Flaring conditions that favour reaction type 1 and reaction type 2 for sweet and sour gas respectively offers least chemical species. In addition, the excess or deficiency of theoretical air, the efficiency of the flare system, the carbon mass content of the fuel in the flare stream and other impurities play an important role in the type and quantity of gaseous emissions anticipated from flaring operation. For policy makers world-wide, especially regions where natural gas flaring is alarming, flaring emission estimates based on reaction type as used in this study could assist in encouraging the allowance of proper operating conditions in flaring operations. This will in turn reduce the type and quantity of chemical species in flaring emissions that can degrade our environment and impact negatively on human health. More so, regular performance evaluation should be done on the flare system by oil and gas companies to ensure efficiencies as

suggested in this work and many other literatures are adhered to by oil corporations.

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