

A CRITICAL REVIEW OF NATURAL GAS FLARES-INDUCED SECONDARY AIR POLLUTANTS

J.A. SONIBARE

*Environmental Engineering Research Laboratory
Department of Chemical Engineering
Obafemi Awolowo University
Ile-Ife, Nigeria*

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*to whom all correspondence should be addressed:

e-mail: asonibar@oauife.edu.ng

ABSTRACT

Application of material balance analysis (in one of our previous studies) to natural gas flare in the upstream petroleum operations confirmed the emission of primary air pollutants in form of CO, CO₂, NO, and NO₂ from “sweet” natural gas while “sour” gas emits SO₂ in addition; incomplete combustion may be an impetus for the release of volatile organic compounds (VOCs) into the atmosphere from this same source. In this article, the significance of these gaseous emissions in the formation of secondary air pollutants in the atmosphere is reviewed for the purpose of air pollution control strategy. The goal is to describe the formation mechanism, to determine the influencing factors in formation along with environmental impacts and to identify the required technological and policy control approach for an improved environmental protection.

KEYWORDS: primary air pollutants, secondary air pollutants, sulphate, nitrate, particulate, ozone.

INTRODUCTION

During upstream petroleum operations, flares are commonly used either for routine or emergency purpose in the removal of associated gas for safe operations. This may be considered a better alternative to vent boom due to the anticipated destruction of natural gas but the resulting several air pollutants identified as emission products from this activity calls for another approach in natural gas removal. Though IPCC (1996) recognized carbon dioxide (CO₂) and water (H₂O) as major output from gas flares, Sonibare and Akeredolu (2004) predicted other products to include carbon monoxide (CO), nitrogen oxide (NO), and nitrogen dioxide (NO₂), from “sweet” natural gas while “sour” gas emits sulphur dioxide (SO₂) in addition. Incomplete combustion may be an impetus for the release of volatile organic compounds (VOCs) into the atmosphere from this same source. These additional products are attributed to the variations in operating conditions of gas flares and the gaseous emissions have degradation potential on the environment either as primary or secondary pollutants.

Sonibare and Akeredolu (2005) identified exposure period and pollutant concentrations as major factors influencing environmental impacts of these flares but the species considered in the study were those formed from the overall chemical reactions of the reaction equations. Kinetic mechanisms of combustion reactions are complex; for instance about 177 reactions steps were identified by Li and Williams (1999) as taking place in natural gas combustion. Though the claim by Strosher (2000) that most of these products are destroyed in the flame before release into the atmosphere could be justified, there is a need for the various products resulting from interaction between the emissions from these flares and atmospheric compositions to be accounted for, if only for environmental protection. In this study, efforts are made to identify some of these products that are of environmental concern.

During photochemical reactions in the atmosphere, free radicals formed including hydroxyl (OH^{*}), hydroperoxyl (HO₂^{*}), methyl (CH₃^{*}), single oxygen (O(¹D)^{*}), and hydrogen (H^{*}) can react with any of the released gaseous emissions from natural gas flares to form new products which are referred to

as secondary pollutants. In addition to radiation intensity which can influence these reactions are temperature and relative humidity (Folberth *et al.*, 2003). The variation of the parameters with different periods of the year signifies the possibilities of concentrations variation of the various new products.

The impacts of air pollution on the environment make this study important for control purpose (Figure 1). Given the restricted availability of observations of some components in the atmosphere, there is always a need for calculated estimate of pollutants supply (EEA, 2003) and adequate knowledge of the species to account for as revealed in this study is considered a positive contribution to environmental protection. The study is expected to assist in protecting the hosts of natural gas flares in the petroleum producing areas of the world, especially the vulnerable sub-populations which may include people with chronic cardiac and respiratory conditions, the elderly, pregnant women, and newborns (Dickey, 2000). Concentration of these pollutants and resulting products of their reactions in the atmosphere is a function of original concentration from sources (Satsangi *et al.*, 2002) and since consumption of some of the gaseous products can affect crop yields (Nelson *et al.*, 2003) while the emitted compounds in the atmosphere can result in deposition (Lightawlers and Cape, 1998) which may encourage the transfer of the pollutants from air to water (Chevalier *et al.*, 2003) or soil and vegetation (Bedell *et al.*, 2003), this study is considered important to assist in providing adequate knowledge in mapping out monitoring strategy for better control implementation and scientifically motivated environmental management.

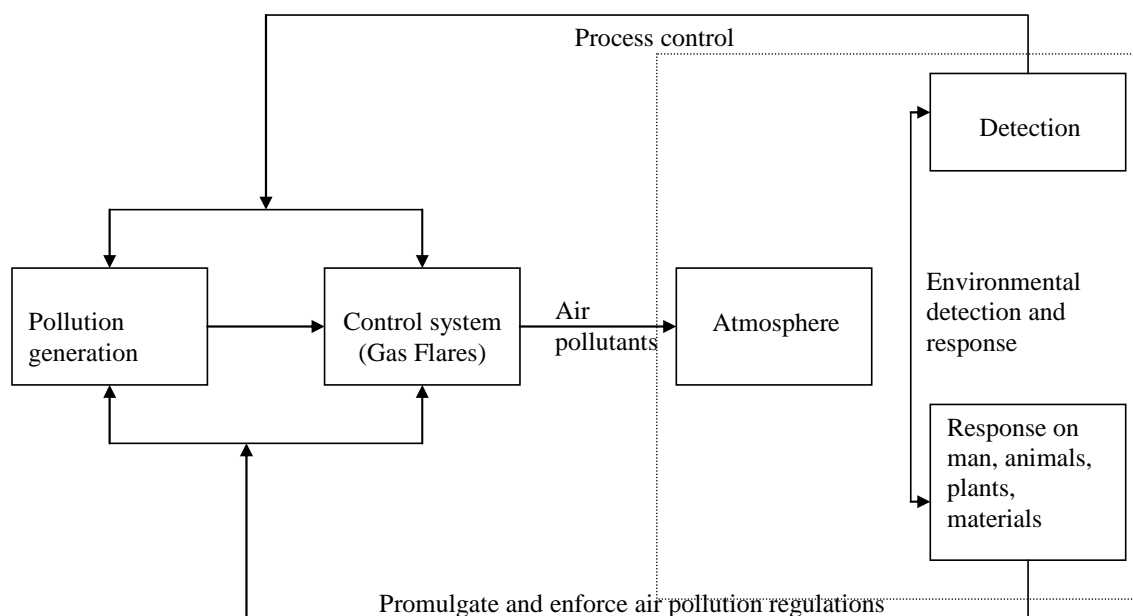


Figure 1. Elements of air pollution generation, prevention and control
(Adapted from Heinsohn and Kabel, 1999)

Soil moisture can be reduced by the presence of some of these gaseous emissions from flare in the soil (Savabi and Stockle, 2001) thus affecting crop yield and nutrients available for crops (Lieferring *et al.*, 2004). There can also be a threat of toxic effect on both vegetation and soil (Beddel *et al.*, 2003). Fevnades *et al.*, (2002) demonstrated the possibility of CO₂ and CH₄ consumption by some crops while Ruth-Balaganskaya and Kudrijalt (2002) confirmed the possibility of sulphur products to become route for sulphur migration in the soil-plant system. Damage that can result from this gaseous emission consumption by vegetation can affect aesthetic value of plants and reduces their economic value as food (Westenbarger and Frisvold, 1994) and fiber. While serving as SO₂ sink in the atmosphere (Johnson and Fegley, Jr, 2002), resulting water can become harmful to vegetation (Cape, 2003) just as the aquatic life can be affected (Havens *et al.*, 1993). A reduction or total elimination of these gaseous emissions from the atmosphere has been identified as a way to reduce soil acidification (Pawlowski, 1997) but this can be done only if there is adequate knowledge on the factors influencing production as set out to be reviewed in this study. This and the global use of gas flares (Figure 2) are the reasons behind this review.

Secondary Air Pollutants

Air pollutants which are substances in the air that could, if present in high enough concentrations, harm humans, animals, vegetation or material may be emitted directly from identifiable sources or produced in the air by interactions among two or more pollutants. While those emitted directly are classified as primary air pollutants, the later are generally termed

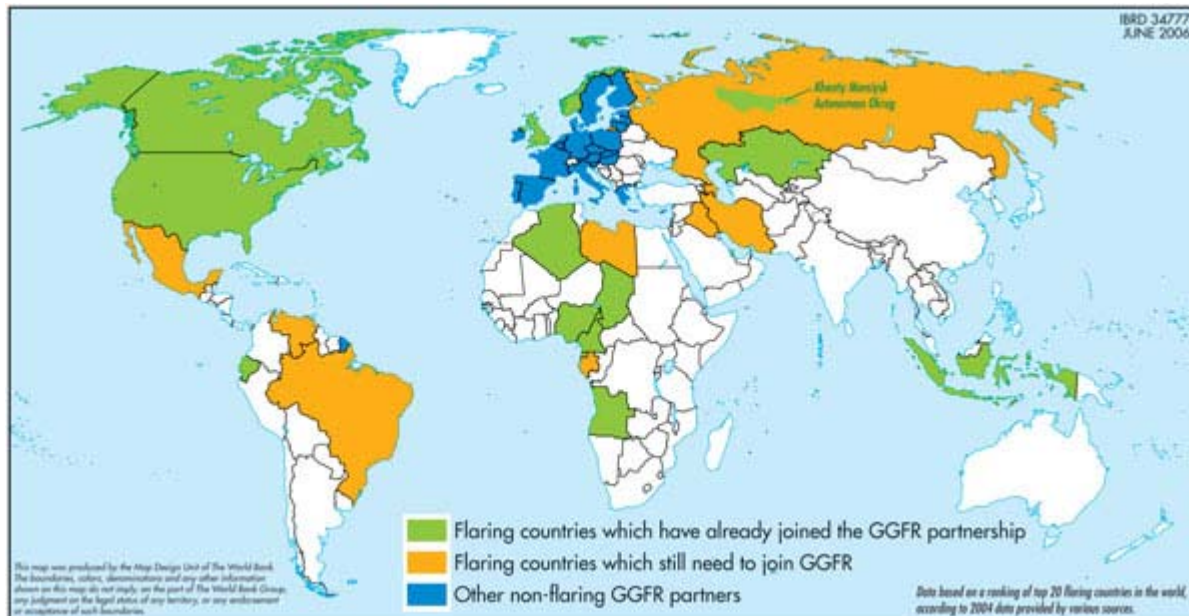


Figure 2. Global use of Gas Flares

secondary. Though the interaction among the primary air pollutants may require photo activation of the sun, this is not a necessary condition like the chemical reactions that must be involved (Jenkins and Clemitchaw, 2000). Secondary air pollutants are the oxidized products resulting from these interactions.

Impacts of the secondary air pollutants depend among other factors on the primary species interacting for their production and the resulting products. Adverse respiratory effects can occur due to their impacts on human (Bernstein, 2004) and some of the products may be toxic (Nazaroff and Weschler, 2004). Extensive literature survey revealed that secondary air pollutants from the products of interactions between earlier identified primary air pollutants in gas flares by Sonibare and Akeredolu (2004) and atmospheric compositions may include acid rain, particulates, and ozone and by inference, impacts of secondary pollutants from the equipment will include those from these three.

Acid rain, a secondary air pollutant which gained prominence in the late 1960s because of its perceived effects on ecosystem integrity (Menz and Seip, 2004) became a key environmental issue in 1980s (Yu *et al.*, 1998). It is from nitrate and sulphate (Irwin *et al.*, 2002) and usually results in the acidification of the environment (Table 1). Interests in controlling its precursors which include SO₂ (Pirjola *et al.*, 1999) and NO_x stems from health concerns, particularly their effects in the form of particulate matter, another secondary air pollutant. The presence of sulphate may influence emission of methane in peat sites (Watson and Nedwell, 1998) thus creating further air pollution problems. Key findings show that acid rain continues to threaten sensitive aquatic and terrestrial ecosystems in some countries of the world (Fenech, 1998 and Peart, 2000) while groundwater can be acidified down to pH 4.4 in the upper 3 – 4 m of saturated zone due to its impact (Kjoller *et al.*, 2004). This indicates that agriculture in such an environment may be negatively affected. Furthermore, at certain temperature, there can be persistent negative effect on net photosynthesis of vegetation (Momen *et al.*, 1999). Sulphuric acid, its major constituent, may impact negatively on historical buildings (Tecer, 1999) and it may decrease cement strength as well as affecting stone monuments made of marble and limestone (Xie *et al.*, 2004).

Table 1. Sulphuric and Nitric Acids as Major Sources of Acidity in Precipitation*

Substance	Concentration in Precipitation (mg L ⁻¹)	Contribution to Free Acidity (microequivalents L ⁻¹)	Contribution to Total Acidity (microequivalents L ⁻¹)
H ₂ CO ₃	0.62	0	20
NH ₄ ⁺	0.92	0	51
Al, dissolved	0.05	0	5
Fe, dissolved	0.04	0	2
Mn, dissolved	0.005	0	0.1
Total organic acids	0.34	2.4	4.7
HNO ₃	4.40	39	39
H ₂ SO ₄	5.10	57	57
Total		98	179

Source: Yen (1999)

When acid seeps into the soil, it may deplete soil minerals such as calcium, magnesium, potassium, and other trace nutrients essential to vegetation nutrition. Deposition of the highest acid concentration near the source as identified by Larseen *et al.*, (1999) signifies the seriousness of the negative impact that the hosts of gas flares in the upstream petroleum operations of the world like the Niger Delta Area of Nigeria might be facing. Raputa *et al.*, (2008) established the presence of both nitrate and sulphate at significant levels around oil-gas flare. Wind blown which is a function of the meteorology of the host area and alkaline soil dust influenced by soil structure and composition are important in neutralizing this acidity of the emissions. In addition, rain acidity attributed to SO₄²⁻ can be neutralized by NH₄⁺ and Ca with the neutralizing factors (NF) determined as (Kulshrestha *et al.*, 1996):

$$NF_{(NH_4)} = \frac{NH_4}{NO_3 + 2SO_4} \quad (1)$$

$$NF_{(Ca)} = \frac{Ca}{2NO_3 + SO_4} \quad (2)$$

$$NF_{(Mg)} = \frac{Mg}{2NO_3 + SO_4} \quad (3)$$

Ozone is formed by the gas-phase oxidation of hydrocarbons and carbon monoxide catalyzed by hydrogen oxide and nitrogen oxide radicals (Jacob, 2000) in the troposphere. In addition to the active participation of NO and NO₂ in acid rain formation is the limiting factor characteristic they display in ozone production (Plummer *et al.*, 1996) where VOCs and CO are oxidized. CO is one of the main reactive trace gases in the earth's atmosphere and it influences the atmospheric chemistry as well as the climate (Badr and Probert, 1995) thus playing important roles in the formation of secondary air pollutants like ozone. Ozone is a strong photochemical oxidant with its elevated concentrations in ambient air causing serious health problems and damage to ecosystems, agricultural crops and materials (EEA, 2002). Due to these, the European Council, in 1992, adopted a directive on air pollution by ozone (EEA, 2001) establishing procedures for harmonized monitoring of ozone concentrations, exchange of information, communication with and alerting of the population and to optimize the action required for its reduction. Ozone plays a significant role in SO₂ oxidation in rainwater especially in the presence of H₂O₂ (Penkett *et al.*, 2007).

Ozone toxicity occurs in a continuum and when in higher concentrations with longer exposure duration, the impacts may be severe (Table 2). A short- term exposure to its concentrations in the range of 120 – 240 µg m⁻³ and higher could lead to decrease in pulmonary function in children, adolescents, and young adults (WHO, 2000). There has been documented evidence that it might interfere with antimicrobial defenses thus promoting chest infections (DOH, 1998). Furthermore, exposure of ecosystems and agricultural crops to certain level of ozone can result in visible foliar injury and in reductions to crop yield and seed production (EEA, 2001a). Huixiang *et al.*, (2005) suggested that the yields of winter wheat grown in the Yangtze Delta in 1999 and 2000 were likely reduced by about 20–30% as a result of damage caused by exposure to ambient ozone while Calatayud and Barreno (2001) reported efforts taken to combat ozone impacts in the reduction of the

yield of several important agricultural crops in Spain. Assuming no change in agricultural production practices, (Wang and Mauzerall, 2004) projected grain loss due to increased levels of O₃ pollution to increase to 2–16% for wheat, rice and corn and 28–35% for soybeans by the year 2020. The associated economic costs are expected to increase by 82%, 33%, and 67% in 2020 over 1990 for China, Japan and South Korea, respectively. To underpin practical recommendations aiming to increase the sustainability of agricultural land management in a changing environment and to secure food supply in regions with rapidly growing populations, Fuhrer and Booker (2003) stressed the need for research on the effects of ozone on agricultural crops and agro-ecosystems. To some vegetation species, the adverse effects can be noted at relatively low ozone levels. Other materials such as natural and synthetic rubbers, coatings and textiles can also be affected by ozone while its synergistic effects in combination with the acidifying components SO₂ and NO₂ have been reported to lead to increased corrosion on building materials like steel, zinc, copper, aluminium and bronze.

Table 2. Threshold Values for Ozone Concentrations*

Threshold for:	Concentration ($\mu\text{g m}^{-3}$)	Averaging Period (h)
Health protection	110	8
Vegetation protection	200	1
	65	24
Informing the population	180	1
Warning the population	360	1

*Source: (EEA, 2001a)

Particulate which is the third secondary air pollutant of importance comes in form of aerosol with SO₄²⁻ and NO₃⁻ as some of the dominant species (Selma *et al.*, 2001, Sun *et al.*, 2004 and Chang and Lee, 2007) if the precursors i.e. primary pollutants are from natural gas flares. NO₂ is precursor to HNO₂ formation which may eventually result in HNO₃ and nitrate aerosol formation (Park *et al.*, 2005) while SO₂ oxidation followed by binary H₂SO₄-H₂O or ternary H₂SO₄-H₂O-NH₃ nucleation usually results in the formation of aerosols (Alastair *et al.*, 2004). In addition to both sulphate and nitrate aerosols are the secondary organic aerosol (SOA) which depend strongly on the conversion of VOCs (Dechapanya *et al.*, 2003) released from the gas flares. Though aerosol formation from primary air pollutants resulting from natural gas flares emissions usually takes place outdoor, the impacts on the environment may include indoor (Gauvin *et al.*, 2002).

They are ubiquitous in the troposphere and of special interest since they contribute to both light scattering and absorption of radiation with consequential visibility and climate effects (Madhavi and Badarinath, 2004; Penner and Novakov, 1996). They also produce brighter clouds that are less efficient at releasing precipitation. These in turn may lead to large reductions in the amount of solar irradiance reaching Earth's surface, a corresponding increase in solar heating of the atmosphere, changes in the atmospheric temperature structure, suppression of rainfall, and less efficient removal of pollutants. The aerosol effects can lead to a weaker hydrological cycle, which connects directly to availability and quality of fresh water (Ramanathan *et al.*, 2001). Chameides *et al.*, (1999) suggested that resulting haze from atmospheric aerosols could depress optimal yields of 70% of the crops grown in China by at least 5–30%. Other impacts may include health which are chronic mortality in adult (Pope *et al.*, 1995) and infant (Bobak and Leon, 1999); asthma and other lower respiratory symptoms in adults (Dusseldorp *et al.*, 1995) and children (Roemer *et al.*, 1993); and chronic bronchitis in both adults (Abbey *et al.*, 1995) and children (Dockery *et al.*, 1993). Based on WHO (2002) global estimates, about 2.5 million deaths each year result from indoor exposures to particulate matter in rural and urban areas in developing countries, representing 4-5% of the 50-60 million global deaths that occur annually. These effects may not be confined to the local area of production but extend at regional as well as global scales due to long transportation of aerosols (Mitra and Sharma, 2002).

FORMATION MECHANISM

Formation of the three identified natural gas flares-induced secondary pollutants can be described with the natural gas flare seen as a stationary source located in an unrestricted environment where it is directly emitting primary air pollutants into the atmosphere through plume (Figure 3). Primarily based on temperature, the atmosphere can be stratified as troposphere, stratosphere, and

mesosphere (Figure 4), with the secondary air pollutants formed depending on the level of interaction between these primary air pollutants and the atmospheric composition which is about 79% nitrogen, 20 % oxygen, and 1% other gases.

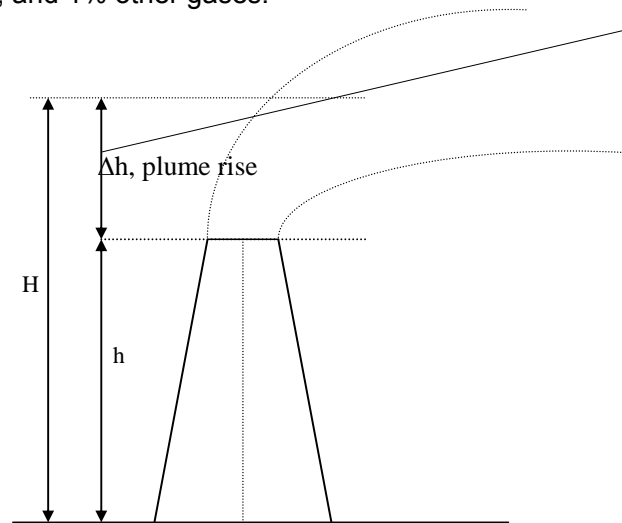


Figure 3. Natural Gas Flare with Plume rise

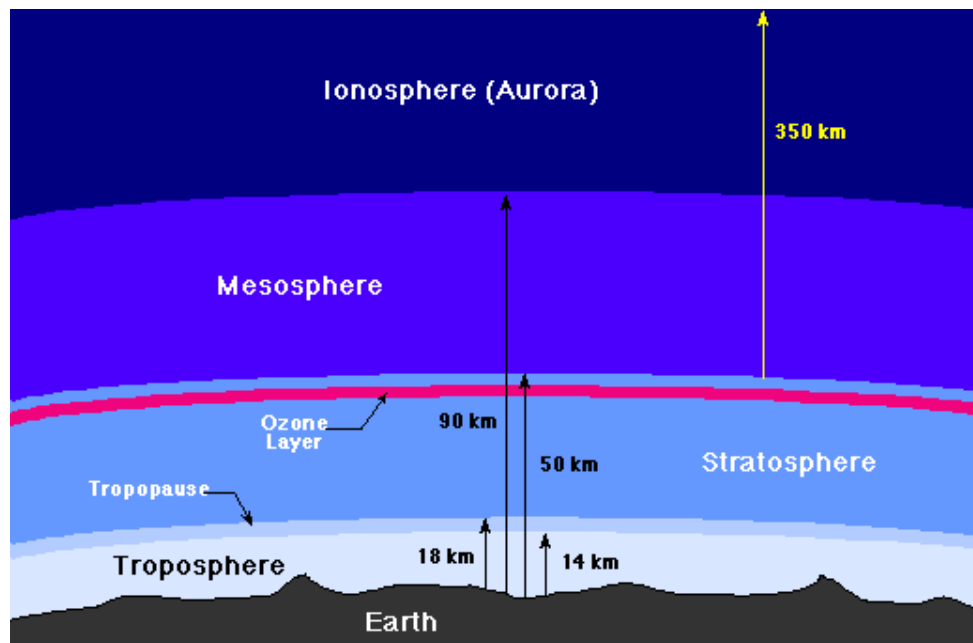


Figure 4. Atmospheric Stratification (<http://csep10.phys.utk.edu/astr161>)

The troposphere is the lowest layer of the atmosphere and the layer between the ground and up to about 15 and 10 km at the equator and poles respectively. There, the temperature decreases at the rate of $6.5\text{ }^{\circ}\text{C km}^{-1}$ with a well mixed air and relatively strong thermally driven convection. It is where all weather takes place and at its top, the air pressure is about 10 % of that at sea level. In the stratosphere, which is the layer between the troposphere and approximately 50 km, there is an almost uniform temperature except in the upper part where it rises to approximately $0\text{ }^{\circ}\text{C}$; this increase is attributed to the absorption of ultraviolet radiation by ozone from the ozone layer located therein. There is a little bulk mixing in this layer because the air flow is almost horizontal. The layer between 50 and 85 km is the mesosphere and in this region, the temperature variation is a linear decrease to approximately 175 km. The uppermost layer of the atmosphere is the thermosphere and it is located above the mesosphere with the temperature increasing to about $1230\text{ }^{\circ}\text{C}$. Many atoms are ionized in the layer thus being labeled the ionosphere. This layer is very thin and is also responsible for absorbing the most energetic photons from the sun. Its structure is strongly

influenced by the charged particle wind from the sun, which in turn, is governed by the level of solar activity.

Table 3. Composition of Atmospheric Air*

Group	Species	Average Concentration (ppm)	Approximate Residence Time
Major Species	N ₂	780,840	10 ⁶ yr
	O ₂	209,460	10 yr
	H ₂ O	Variable	
Inert Gases	Ar	9,340	
	Ne	18	
	He	5.2	
	Kr	1.1	
	Xe	0.09	
Trace Species	CO ₂	350	15 yr
	CH ₄	1.72	10 yr
	H ₂	0.58	10 yr
	N ₂ O	0.33	150 yr
	CO	0.05 – 0.2	65 days
	NH ₃	0.01	20 days
	NO/NO ₂		
	Remote Regions	< 0.00004	1 day
	Rural continental United States	0.00002 – 0.00005	1 day
	Urban	0.001	1 day
	O ₃ (troposphere)	0.02 – 0.05	< 1 year
	H ₂ O ₂	0.001	
	HNO ₃	0.001 – 0.0001	1 day
	HCs	0.001 – 0.050	
	HCHO	<0.0005 – 0.00075	
	HCOOH	>0.02	
CH ₃ OH	0.04 – 0.06		
CFC 11	0.003	65 yr	
Sulphur compounds	SO ₂	0.0002	40 days
	COS	0.0005	> 0.03 x 10 ⁵ h
	CS ₂	0.00001 – 0.0002	> 1.8 x 10 ⁵ h
	CH ₃ SH		3 – 13 h
	(CH ₃) ₂ S		31 h
	H ₂ S		53 h
Free radicals	OH*	1–10 x 10 ⁶ molecules cm ⁻³	
	HO ₂ *	1 x 10 ⁹ molecules cm ⁻³	

*Source: Heinsohn and Kabel (1999)

Depending on the altitude, temperature, and radiation wavelength, initiation reactions take place in the atmosphere in form of photolytic reactions from where other stages of the reactions set in. The other three general steps in formation mechanism are propagation reaction, branching reaction, and terminating reaction with production of radicals of various forms which include: hydroxyl (OH*), hydroperoxyl (HO₂*), methyl (CH₃*), single oxygen (O(¹D)*), and hydrogen (H*) . Any of these radicals may react with emission products from natural gas flares for the formation of secondary products that may be of environmental concern. Considering the interaction between primary air pollutants released from natural gas flares (Sonibare and Akeredolu, 2004) and the various atmospheric compositions (Table 3) in each of the layers, a review of the reaction mechanism of the resulting secondary air pollutants is undertaken below:

i. Acid Rain

Through a series of complex chemical reactions, SO₂ and NO_x emitted by natural gas flares are converted to acids that may result in rain acidity. Photochemical processes, because of their production of radicals, are strongly coupled to SO₂ to form H₂SO₄ (Song *et al.*, 2003):



According to Gundel *et al.*, (1994), the reaction usually involves several atmospheric reactions which may include those heterogeneous reactions taking place within fog as:



The catalyst in equation (5) above may be ammonia and when this is the case, rapid acidic component of the atmosphere may be produced in the conversion process (Renard *et al.*, (2004).

Likewise, nitric acid formation in the atmosphere is generally by reactions of NO from the gas flares with both the hydroxyl and hydroperoxyl radicals while the conversion of NO₂ is usually achieved via a one step mechanism into inorganic nitrate (Bottenheim *et al.*, 1984):



This formation of nitric acid is a function of the time of the day:

(During daytime)



(At night)



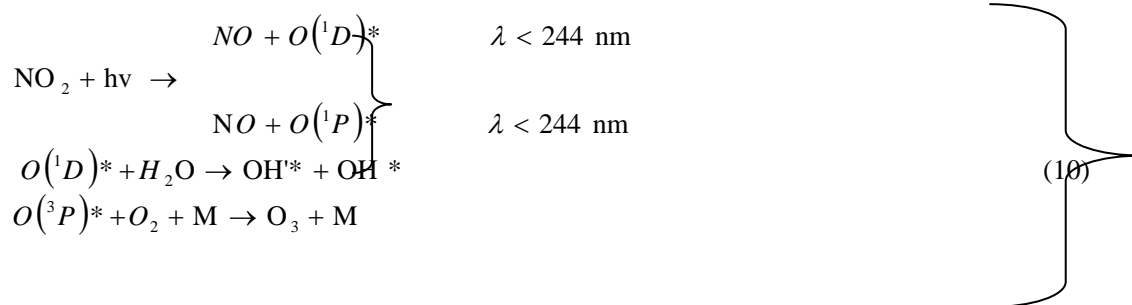
Though formation and deposition of nitric acid on surfaces is a popular irreversible sink of nitrogen oxides (NO_x), the reaction of nitric oxide with nitric acid may convert HNO₃ to photochemically active NO_x (Knipping and Dabdub, 2002) in the atmosphere. If nitrous acid is formed during the conversion stage, this is usually oxidized to nitric acid by O₂, O₃, and H₂O₂ in aqueous solution (Damschen and Martin, 1983; Calderon *et al.*, 2008). To fully understand the status and mechanism of acid rain, it is important to know the pH of precipitation and its chemical constituents (Okuda *et al.*, 2005) in the area of interest over a period of time.

ii. Ozone

In the atmosphere, three major sources of ozone may include the stratosphere, the free troposphere, and the boundary layer photochemical reactions (Derwent and Kay, 1988) with the direct formation generally being the reaction:



where M is a molecule such as N₂ or O₂ whose participation is necessary to conserve energy and momentum. Several reactions and processes are required via initiation, propagation, branching before the termination stage represented in equation (9). The troposphere alone where ozone is produced as a secondary air pollutants harbors about 59 reactions and 23 species for this purpose (Heard *et al.*, 1998). The necessary ingredients for the formation are sunlight, volatile organic compounds, and nitrogen oxides (NO/NO₂). Summarily, it is formed by photolytic reactions of NO₂ via the reaction of oxygen radical with O₂. During this process, the O(¹D)* radical reacts with water vapour to produce hydroxyl radicals (OH*) or with methane to form methyl and hydroxyl radicals which play active role in the formation of other pollutants:



As sunlight becomes more intense later in the day, nitrogen dioxide is broken down thus increasing the concentration of ozone. Like the peroxy radicals, the main role of VOCs (volatile organic compounds) is to prevent the ozone formed from being immediately consumed by NO to produce NO₂ in the following reaction (Curtiss and Rabl, 1996):



However, as sun disappears, the production of ozone is halted (Kumar and Mohan, 2005) while the remaining ozone in the atmosphere may then be consumed by several different reactions thus resulting in downward concentration. Ozone episodes with concentrations above 50 ppb are quite frequent and its formation is to a large extent limited by the emissions of NMVOCs (NEGTA, 2001).

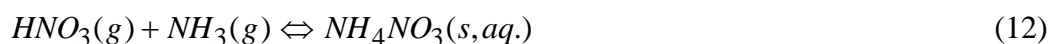
iii. Aerosols

The presence of aerosols in the atmosphere is very important because of the various associated impacts and this has necessitated continuous studies of their formation mechanism for effective control strategy. Primary air pollutants of interest from natural gas flares for the formation of aerosols include NO/NO₂, SO₂, and volatile organic compounds with nitrate, sulphate, and secondary organic aerosols respectively as resulting aerosols and the conversion is usually due to gas-to-particle conversions (Funasaka *et al.*, 1999). An essential prerequisite for any of these gases to particle conversions is the presence of the species in the gas phase at a partial pressure in excess of its saturation vapour concentration with respect to the condensed phase (i.e. condensable material). In the experimental and model studies by Sarwar *et al.*, (2003), it was demonstrated that secondary particle mass concentrations increase substantially with lower air exchange rates.

Generally, important aerosol formation processes include nucleation, condensation, and coagulation but Kermiren and Wexler (1995) indicated that for real growth to be experienced, aqueous-phase reactions in droplets or aerosol particles and reactions taking place at the interphase of two phases are additional stages. However, Clement and Ford (1999) identified an initial growth phase before the coagulation. Nucleation, the important first step in atmospheric aerosol formation may be affected by some factors like ion-induced and homogeneous nucleation, depletion of nanoparticles and ions on the pre-existing aerosol, nano-kohler growth function, the molecule-particle interception geometry, quantum retardation of sticking, electric charges of particles, molecular dipole moments, and the polarization interaction. Whatever the formation mechanism, meteorological parameters have been identified as some of the very strong factors influencing aerosol formation (Hrdličková *et al.*, 2008). For the purpose of the set goals of this review work, the important reaction mechanism for nitrate, sulphates, and secondary organic aerosols are discussed below:

a. Nitrate

This is a very key secondary particulate generally formed as a result of atmospheric reactions of NO/NO₂ involving gas to particle conversion (Michalski *et al.*, 2004). In the lower troposphere, oxidized NO (Eqn. 7) and the emitted NO₂ from natural gas flares react with ozone to produce nitrate compound (Eqn. 8). The HNO₃ produced from this reaction between N₂O₅ and H₂O predominantly occurs in the cloud water and on the surface of particulate, involving the "charge transfer" or "ionic" intermediate NO₂⁺NO₃⁻, with the product being nitrate aerosol and not gaseous HNO₃. However, in the presence of ammonia, ammonium nitrate is formed as secondary aerosol by gaseous HNO₃ (Eqn. 12). In addition to ambient temperature, ammonia concentration influences the aerosol formation (Russel *et al.*, 1983). When required precursors for the formation of ammonium nitrate are absent, heterogeneous reactions on the existing particles take predominant in the fine mode formation (Matsumoto and Tanaka, 1996).



b. Sulphate

Apart from the nitrates, another important form of secondary aerosol is the sulphate which is principally formed from atmospheric conversion of SO_2 produced by the natural gas flares. Its formation is usually either in the gas (Eqn. 13) or aqueous phases (Eqn. 14) with hydroxyl and hydroperoxyl radicals as important reacting agent (Stein and Lamb, 2003):

The gas phase :



The aqueous phase :



Formation of new nuclei in sulphate aerosols is expected to be mainly the result of binary homogeneous nucleation of sulphuric acid/water droplets. This nucleation rate is a function of vapour phase acid mass concentration, the atmospheric relative humidity, and temperature. When there is a decrease in temperature but increase in both concentration and relative humidity, there can be significant increase in nucleation rate (Clement and Ford, 1999). Condensation on existing aerosol is a mechanism that may compete with nucleation. Though aqueous phase oxidation is the predominant mechanism for sulphate formation under fog conditions followed by condensation of the H_2SO_4 system, nucleation burst ascribed to high local sulphuric acid concentration by Lazaridis and Skouloudis (1999) may cease new particle formation.

c. Secondary Organic Aerosols (SOAP)

Certain classes of VOCs are more likely to lead to aerosol formation by their general high reactivity and types of oxidation products. Some of these VOCs are emitted by flare while the resulting aerosols are SOAP. Winiwarter and Puxbaum (2003) summarized the SOAP formation pathway as shown in Figure 5. When the strong oxidants (O_3 , hydroxyl, and nitrate radicals inclusive) react with the VOCs in the atmosphere, the stable molecule is broken down to form new radicals. These new radicals rapidly undergo a chain of reactions to form new compounds some of which have considerably lower volatility than the original VOCs. At sufficiently high partial pressure, the resulting condensable organic carbon can be converted into particulate phase while further agglomeration reactions possibly increase the molecule size at the same time decreasing volatility and ultimately fixing the molecule to particulate phase. These compounds are always fine in nature and may result in elevated $\text{PM}_{2.5}$ concentrations of an area as observed by Brook *et al.*, (2004).

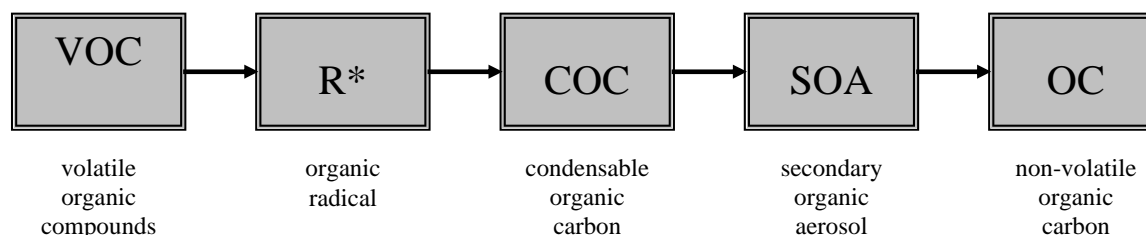


Figure 5. Secondary Organic Aerosol (SOA) Formation Pathway

Control Implications of Flare-Induced Secondary Air Pollutants Formation in the Atmosphere

Without the possible impacts of the secondary air pollutants capable of being formed in the atmosphere by primary air pollutants from natural gas flares as highlighted in this review, Akeredolu and Sonibare (2004) reported that the environmental degradation potential of flares in terms of gaseous concentration is directly proportional to the gaseous concentration emitted. The requirement of these gaseous concentrations as active ingredients in secondary air pollution formation as shown in the formation mechanism review is an indicator that a total control on the emissions from flares may be a significant way of limiting flare-induced secondary air pollutants to

the least possible level. Various difficulties including trans boundary air pollution and life time of primary pollutants that may be encountered in the control of atmospheric compositions strongly support this. Though NO has a very short life time thus may not encourage regular formation of secondary pollutants, the long life time of SO₂, CO, and CO₂ which is about 3 days, 30 days, and 4 years respectively (Glazunor *et al.*, 2001) indicates an otherwise situation.

The control of gaseous emissions from natural gas flares can be addressed in two ways: technology and policy. In using technology approach, the focus will be on the gas flare equipment releasing the primary air pollutants. For instance, IPCC (1994) and IPCC (1996) indicated that the state of combustion equipment plays prominent role in the nature of their emission products, an indication that a good maintenance culture may reduce the concentration of primary air pollutants coming from natural gas flares during the combustion activities. Likewise, the conclusion of Sonibare and Akeredolu (2004) that the operating conditions of natural gas flares are strong enough to determine the type of primary air pollutants released as emission products makes it mandatory for the operators of these gas flares in the oil fields to be conscious of suitable operating conditions that will reduce the number of gaseous species released at a point in time. Effective control of operating gas flare operating temperatures may be an indirect way of controlling NO_x emissions which may be a way of reducing the formation of both acid rain in form of HNO₃ and aerosols in form of nitrate. In the process of piping natural gas into the flare boom, the knockout drum is a necessary route that must be taken for liquid removals (Akeredolu and Sonibare, 2004) to encourage efficient combustion and preserve the life of flare boom. If this removal approach can be applied to sour gas for sulphur compounds removal then, it may be possible to prevent SO₂ formation thus eliminating it from the species of primary air pollutants. The use of fuzzy logic to constantly monitor the efficiency of the removal approach as demonstrated by Lia *et al.*, (2008) can assist greatly in achieving the desired level. Like in the NO_x control, absence of SO₂ from the primary air pollutants is a way to control acid rain and aerosols formation but in form of both H₂SO₄ and sulphate respectively. Furthermore, the removal technology can be extended to flue gas in form of gas scrubbers for the removal of both NO_x and SO₂ but this may be cost intensive if at all technologically feasible.

Policy option in controlling the formation of flare-induced natural gas flares may require the inputs of every stakeholder. Though atmospheric compositions may be difficult to control as mentioned earlier, the use of appropriate policy formulation may assist to some level. Active radicals are required in the atmosphere to react with these primary air pollutants in the formation of secondary pollutants thus any policy that may result in the reduction of these radicals formation is an indirect way of control. For instance, hydroxyl radicals are very important in the formation of these pollutants thus whatever will discourage their formation in the atmosphere can reduce their impacts in the formation activity. NH₄NO₃ and ammonium sulphate (NH₄SO₄) are very common secondary aerosols but their formation can be controlled if the key agents are not encouraged to react. Even if NO_x and SO₂ are released into the environment, the absence of NH₃ is a way of putting these aerosols formation to a check. Cattle dung which is a common source of NH₃ may be avoided and a policy discouraging cattle rearing around natural gas flare installations may be an effective way of using policy formulation to control these secondary aerosols formation. Since the secondary air pollutant formation mechanism depends strongly on the primary air pollutant presence and concentration, a policy that encourages profitable use of associated natural gas thus eliminating natural gas flares may be a most effective way of control. For example, upstream petroleum producers may be made to pay market price of natural gas or LPG (which ever is most costly) for every cubic metre of gas flared while incentives should be given to profitable utilizing operators.

Conclusion

Three important secondary air pollutants formed in the atmosphere due to the presence of primary air pollutants from natural gas flares have been reviewed with their environmental impacts and formation mechanisms discussed for the purpose of control measures. It has been shown that these secondary air pollutants can affect man, vegetation, and other materials thus leaving both health and economic impacts to tackle. Various factors required in the formation of these secondary air pollutants showed that the control of emissions of the primary air pollutants may be the easiest way to minimize the formation of the secondary air pollutants; both technology and policy options were considered.

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