



ENVIRONMENT MANAGEMENT: PARTICULATE MATTER FROM REFINERY FLARES AND HEALTH EFFECTS OF SOOT

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Abstract

Flaring is a high-temperature oxidation process used to burn combustible components, mostly hydrocarbons, of waste gases from industrial operations. Smoking results from combustion, depending upon waste gas components and the quantity and distribution of combustion air. Waste gases containing heavy hydrocarbons such as paraffins above methane, olefins, and aromatics, cause smoke.

New scientific evidence has led to recognition of the significant role of black particles (black carbon or soot) as one of the short-lived climate forcers. Measures focused on black carbon and methane are expected to achieve a significant short-term reduction in global warming. If they were to be implemented immediately, together with measures to reduce CO₂ emissions, the chances of keeping the earth's temperature increase to less than 2°C relative to pre-industrial levels would be greatly improved. The same measures would also directly benefit global health and food security. An external momentum force, such as steam injection is used for efficient steam/waste gas mixing and turbulence, which promotes smokeless flaring of heavy hydrocarbon waste gas. In Oil and Gas industry, all the tail gas containing H₂, CO, CO₂ and C₂ to C₅, vary its composition and smoke cannot be seen some times but unburnt hydrocarbon escapes.

Key Words: Black Carbon, Flares, Green House Gases, Poly Aromatic Hydrocarbons, Soot, Waste gases.

Introduction:

Flaring is a technique used extensively in the oil and gas industry to burn unwanted flammable gases. Oxidation of the gas can preclude emissions of methane (a potent greenhouse gas); however flaring creates other pollutant emissions such as particulate matter (PM) in the form of soot or black carbon (BC)^[1]. As of the end of 2011, 150×10^9 cubic meters (5.3×10^{12} cubic feet) of associated gas are flared annually. That is equivalent to about 25 per cent of the annual natural gas consumption in the United States or about 30 per cent of the annual gas consumption in the European Union.^[2,5]

As of 2010, 10 countries accounted for 70% of the flaring, and twenty for 85%. The top ten leading contributors to world gas flaring in 2010, were (in declining order): Russia (26%), Nigeria (11%), Iran (8%), Iraq (7%), Algeria (4%), Angola (3%), Kazakhstan (3%), Libya (3%), Saudi Arabia (3%) and Venezuela (2%).^[3]

That amount of flaring and burning of associated gas from oil drilling sites is a significant source of carbon dioxide (CO₂) emissions. Some 400×10^6 tons of carbon dioxide are emitted annually in this way and it amounts to about 1.2 per cent of the worldwide emissions of carbon dioxide^[4].

Unlike carbon dioxide and other greenhouse gasses, which can survive in the atmosphere for decades and centuries,



black carbon has a relatively short life span of approximately one to two weeks. Black carbon is part of a group of pollution sources known as Short-Lived Climate Forcers (SLCFs), including methane gas and ozone, which are produced on earth.

During their lifetime, black carbon particles are coated with airborne chemicals, which laboratory tests have shown can act like lenses capable of increasing the ability of the particles to absorb sunlight and heat the atmosphere.

What is Soot?

A black powdery substance that consists mainly of carbon and is formed through the incomplete combustion of wood, coal, diesel oil or other materials.

Why Soot is Black?

Because it absorbs energy from sunlight rather than reflecting it, Soot is believed to be a cause of global warming, especially when it settles on snow and ice, reducing their reflectivity.

Soot formation pathway:

Smoke burns up in high temp region [smokes if soot exits this region before being consumed]. Smoke forms when C-C bonds in hydrocarbon crack and aromatic structures grow in to multi ring molecules [>3 ring=primary soot particle]. Other Polyaromatic hydrocarbons [PAH] form a long reaction route to soot. The optimal combustion of fuel at high temperature, such as the current low-sulfur fossil diesel fuel in modern diesel engines, results in the emission of large numbers of very small soot particles (aerodynamic diameter 1–5 nm) that rapidly grow in size (10–100 nm) in (fig-1) the tail pipe by coagulation to form aggregated chains (fig-2), and further by condensation of the simultaneously released semi-volatile organic substances on their surfaces in the atmosphere.

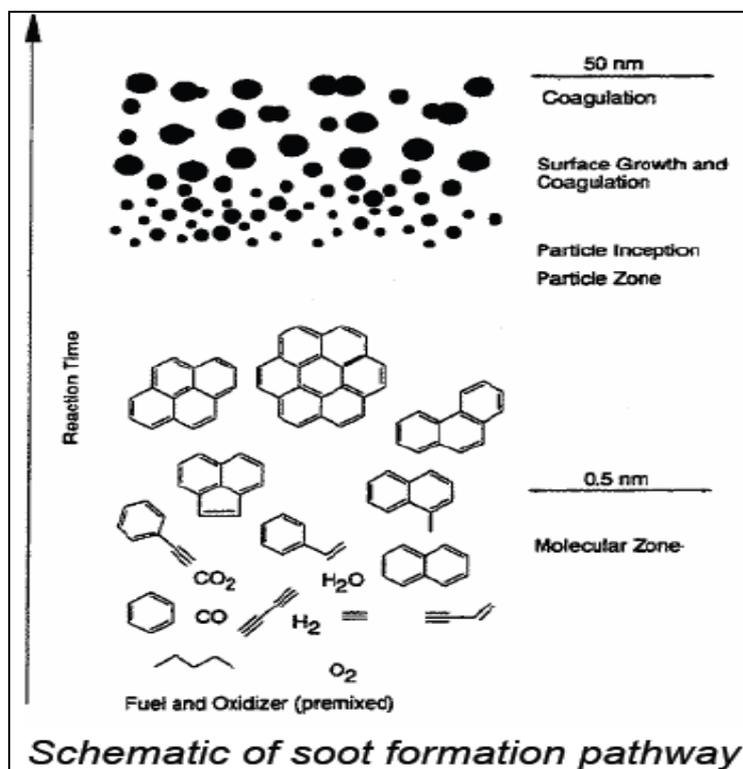




Figure-1

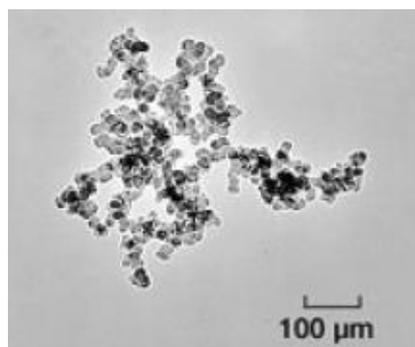


Figure-2

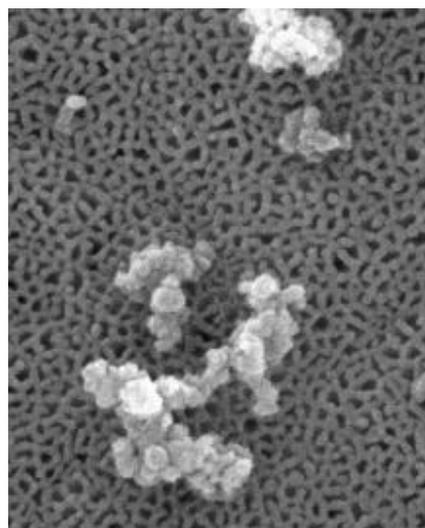


Figure-3

Particulates:

Small, solid particles and liquid droplets are collectively termed “particulates”. These are present in the atmosphere in fairly large numbers and some times pose a serious air pollution problem. The most important physical property is size. Particulates range in size from a diameter of 0.0002 μ (about the size of small molecule) to a diameter of 500 μ with life times varying from a few seconds to several months. This life time depends upon the size and density of the particles and turbulence of air. The number of particles in the atmosphere varies from several hundreds per cm³ in clean air to more than 100,000 per cm³ in highly polluted area. The particulates possess large surface areas in general and hence present good sites for sorption of various inorganic and organic matter.

Inorganic Particulate Matter:

Metal oxides comprise a major class of inorganic particles in the atmosphere. They are produced whenever fuels containing metals are burnt. They are produced whenever fuels containing metals are burnt.

Organic Particulate Matter:

It occurs in a wide variety of compounds in the atmosphere. A typical average formula of a benzene- extractable fraction of organic particulate matter is C_{32.4} H₄₈ O_{3.8} S_{0.083} (halogen)_{0.065} (alkoy)_{0.12}. The bulk of this organic matter is in the respirable 1 μ range.

Polycyclic aromatic hydrocarbons (PAH) are important components of organic particulate matter because of their carcinogenic nature. Some typical PAH compounds are: benzo (α -) pyrene, Chrysene, benzofluoranthene. PAH compounds occur in urban atmospheres at levels of about 20 μ g/m³. They are mostly found in the solid phase. It is known that most PAH compounds are sorbed onto soot particles. Soot itself is a highly condensed product of PAH compounds. A soot particle consists of several thousand interconnected crystallites which are made up of graphitic platelets. The latter (platelets) consist of roughly 100 condensed aromatic rings. Soot consists of 1-3% H and 5-10% O trace metals such as Be, Cd, Cr, Mn, Ni, and V and also toxic organic such as benzo (α -) pyrene adsorbed on its surface. This is shown in (fig-4)

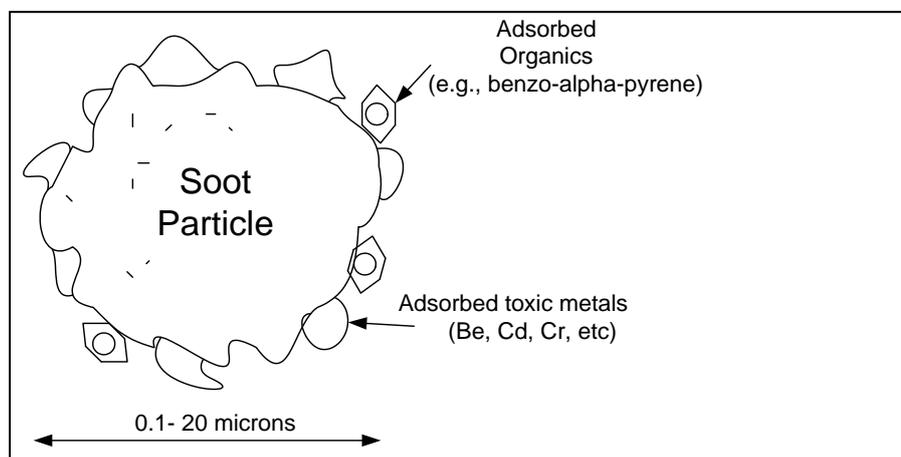


Figure-4

Emission factors:

For a very rough order of magnitude estimate, considering gas flared volumes of 139 billion m³/year as estimated from satellite data [6] and estimating a single valued soot emission factor of 0.51 kg soot/103 m³, flaring might produce 70.9 Gg of soot annually. This amounts to 1.6% of global BC emissions from energy related combustion, based on estimates of 4400 Gg for the year 2000 [7].
 Soot in concentration values [8]:
 Non smoking flares, 0µg/L;
 Lightly smoking flares, 40µg/L;
 Average smoking flares, 177 µg/L; and
 Heavily smoking flares, 274µg/L.

Soot Load Measurement

Measurement of soot can be accomplished using a number of different methods. Below is a general review [9] of each:

• **Thermogravimetric Analysis (TGA)** - This widely accepted technique provides the most accurate estimate of the concentration of soot as a percent by weight. The test involves progressively heating the sample in a nitrogen-rich atmosphere over time to vaporize volatile fractions until the weight of the sample levels off, typically occurring at around 600° C. Then, the nitrogen environment is replaced by air and the temperature is further raised allowing the oil to oxidize until the weight again stabilizes. Soot concentration is then calculated by subtracting the weight of the volatile ash components from the weight of the original sample.

Infrared Analysis - Infrared Analysis has become very popular for measuring soot concentration. Results seem to correlate very well with TGA and the technique is relatively low cost, especially with the proliferation of labs now offering Fourier Transform Infrared (FTIR) analysis. There are also several reasonably priced on-site instruments available for soot measurement. Essentially, soot absorbs infrared energy. Unlike many parameters measured with FTIR, soot creates a broadband change in absorption (baseline shift). So, FTIR instruments generally search for soot in 2000 wave number region. That region is relatively clear of interference from other oil constituents or contaminants making soot measurement relatively easy. The primary interferences related to this method include the disproportionately increasing absorption of infrared energy as soot particles increase in size, and other particles, like dirt, also absorb broad-band infrared energy and are indistinguishable in measurement from soot.

• **Insolubles Test** - This test involves the separation of insolubles from the oil after it has been mixed with various solvents like pentane and toluene. The pentane or toluene insolubles are removed by high-speed centrifugation or by filtration onto a membrane disc. When centrifuged, the insolubles are measured as either mass or volume. When filtered, the weight of the new filter is subtracted from that of the prepared filter to determine weight. The technique is relatively inexpensive and very well established. The main drawback is that all insolubles are measured together, not just the soot. Also, the solvent selected affects the outcome. If pentane is used, organic oxides are included in the measurement of total insolubles. Toluene leaves the organic oxides dissolved.



• **Light Extinction Measurement (LEM)** - The LEM method, researched by Analysts, Inc., method involves casting light at the visible and near infrared frequencies through an object area containing a volume of oil. The light obscured by the oil, as measured by the voltage drop across the object area, is purported to vary with soot concentration. This technique offers simplicity, low cost and a quantitative result. The major drawback lies in the fact that anything that blocks or scatters light is subject to inclusion in the soot estimate (e.g., particles, water, air bubbles, insoluble oxidation by-products, etc.).

• **The Blotter Method** - This sample method requires only a drop or two of oil on standard chromatography paper. The insolubles separate from the oil and provide a quick visual identification of soot. Further, the paper can be diluted in different solvents to provide an indication of the different insolubles present in the sample. The blotter method offers elegant simplicity, but fails to quantify soot concentration. However, a trained eye can estimate concentration given enough experience; but still, any quantification of soot load must be viewed as suspect.

Health Effects of Soot:

Soot particles in the air are a contributing factor in respiratory diseases. The fine particles ($<3\mu$) are the worst causes of lung damage due to their ability to penetrate into the deep air passage. Larger particles ($>3\mu$) are trapped in the nose and the throat from which they are easily eliminated, but finer particles can stay intact for years in the inner most regions of the lungs, which have no effective mechanism for particle removal. The lodged particles in the lungs can cause severe breathing trouble by physical blockage and irritation of the lung capillaries.

Emissions of fine particulate matter (PM and ultrafines) in diesel exhaust have been of growing community, industry and government concern. Their combination of extremely small size and chemical composition increases the likelihood that particles will carry irritants and toxic compounds into the deepest and most sensitive areas of the lungs. This can lead to severe bronchial problems and increased susceptibility to respiratory infection, such as pneumonia, bronchitis, and asthma. Carbon soot particles from diesel engines adsorb onto their surfaces other metals and toxic substances produced by diesel engines such as cancer-causing aldehydes (like formaldehyde) and polycyclic aromatic hydrocarbons (PAH). Occupational health studies link cancers, particularly lung cancer to diesel exhaust exposures. Traffic studies suggest increased rates of respiratory and cardiovascular disease and risk of premature

death near busy urban streets or highways and thus must be addressed by industry and government.

Conclusions

Soot particles can penetrate deep into the lungs and have been linked to a wide range of serious health effects, including premature death, heart attacks, and strokes, as well as acute bronchitis and aggravated asthma among children. EPA's proposal would strengthen the annual health standard for harmful fine particle pollution (PM_{2.5}) to a level within a range of 13 $\mu\text{g}/\text{m}^3$ to 12 $\mu\text{g}/\text{m}^3$ ^[10]. The current annual standard is 15 $\mu\text{g}/\text{m}^3$. The proposed changes, which are consistent with the advice from the agency's independent science advisors, are based on an extensive body of scientific evidence that includes thousands of studies – including many large studies which show negative health impacts at lower levels than previously understood. By proposing a range, the agency will collect input from the public as well as a number of stakeholders, including industry and public health groups, to help determine the most appropriate final standard to protect public health.

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