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Environmental Significance of the Combustion of Liquid Petroleum Fuels: A Review

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Abstract: Since the time of the Industrial Revolution, there has been a dramatic increase in human dependence on energy derived from fuel combustion. Yet, environmental pollution derived from liquid fuel combustion threatens human health and endangers plant and animal lives. Also, the associated corrosion sentences material resources to waste. An understanding of the undesirable pollutant chemical reactions, their products as well as their pollution and corrosion in the environment, is therefore, of prime importance as a prerequisite for addressing the challenges. The review paper examines the chemical reactions and the environmental significance of pollutant products from the combustion of liquid petroleum fuels, as well as the way forward in terms of measures to contain the pollution and corrosion effects and alternative energy sources.

Key words: Combustion, liquid petroleum fuels, pollution, corrosion

INTRODUCTION

From ancient times, health problems are related to air pollution. Anthracosis, or black lung disease, has been found in mummified lung tissue. There is a widespread belief that contemporary air pollutants are involved in the increases in asthma. Air pollution also affects materials in the urban environment. Soiling has long been regarded as a problem.

Air pollution was originally the result of the smoke from wood or coal fires. But, it is now increasingly the result of fine black soot from diesel exhausts. The production of energy from combustion and the release of solvents is so large in the contemporary world that it causes air pollution problems of regional and global nature. Solvents, such as Carbon Tetrachloride (CCl_4) and the aerosol propellants Chlorofluorocarbons (CFCs), are now detectable all over the globe and responsible for problems such as ozone layer depletion.

Similarly, formaldehyde from insulating foams causes illnesses and adds to concerns about exposure to a substance that may induce cancer in the long run. In the last decade, it has become clear that radon leaks from the ground can expose some members of the public to high levels of this radioactive gas within their own homes. Cancers may also result from the emanation of solvents from consumer products - glues, paints and mineral fibres (asbestos). More generally, these compounds and a range of biological materials-animal hair, skin, pollen spores and dusts-can cause allergic reactions in some people. At one end of the spectrum, these simply cause annoyance, but in extreme cases, such as found with the bacterium *Legionella*, a large number of deaths can occur (Tedder *et al*., 1975; Spedding, 1974).

Coal, natural gas and liquid petroleum fuels for heating purposes are classified as primary fuels because they require relatively little pretreatment (apart from the simple physical separation process of distillation) before use. Natural gas occurs alone or in association with coal or crude petroleum. Its main constituent is methane (CH_4), which varies between about 70 and 95% by volume, depending on the source.

Liquefied Petroleum Gases (LPG) include both propane (C_3H_8) and butane (C_4H_{10}) and are particularly suitable for portable applications, as they are readily liquefied under pressure. Gasoline (petrol), kerosine and gas oil (diesel) are different fractions and products of fractional distillation of crude oil. Gasoline, the most volatile of the liquid petroleum fuels, is used almost exclusively in automobile spark-ignition engines. Kerosine is the main domestic heating fuel in Britain, Australia and some other countries. A similar fuel is used as Aviaton Turbine Kerosine (ATK) for sub- and super-sonic jet aircrafts. Gas oil is the main domestic heating fuel in Europe, the United States of America (USA) and Canada. Under its automotive name, diesel fuel, it is used widely in the United Kingdom (UK) and abroad for powering road transport, particularly public and goods vehicles (compression-ignition engines) (Eneh, 2011a).

Fuel oil, predominantly a non-distillate fuel, comprises the residual material from the crude oil distillation processes, the cracking processes and materials discarded during production of lubricating oils. Several grades are marketed and are classified primarily according to their viscosity. The sulphur content of these residual fuel oils has been of concern because of the corrosive effects of the combustion products. It is now attracting renewed attention because of tightening pollution-emission regulatory requirements.

The combustion of a fuel results to fire, which generates heat. The fire may be flame, as in the case of kerosine or gas burning in stove. It may not be flame, as in the case of gasoline or diesel burning in engine or food burning in the body. The generated heat-a form of energy-serves to energize the stove, to perform the work of cooking; the engine, to drive the machine; or the body, to do work. Continuous combustion technology deals with flames, while transport technology deals with gasoline and diesel engines (Al-Khairi *et al*., 2011; Naveenchandran *et al*., 2011; Firmansyah and Aziz, 2011).

Francis Bacon's experiments with the structure of the candle flame possibly began the slow revolution in the understanding of combustion technology and heat. These studies were instrumental to Antoine Lavaoisier's publication in 1777, Reflexions sur la Phlogistique, which began to lay not only the foundations of a quantitative theory of heat, but indeed the basis for the whole of modern chemistry.

James Joule did a well known and important work on the equivalence of heat and energy. This work led to the first law of thermodynamics, which states that energy can neither be created nor destroyed, but can be transformed from one form to another. Thus, the relationship of the quantity of heat added to a system to raise its internal energy and to also do outside work has been expressed in several researchers, including Ibemesi (1998).

The Scottish inventor and mechanical engineer, James Watt improved the Newcomen steam engine, leading to fundamental changes brought by the Industrial Revolution (Lira, 2001). According to Maddison (2003), the Industrial Revolution marks major changes in agriculture, manufacturing, mining, transportation and technology, with a profound effect on the socioeconomic and cultural conditions of people. Most notably, average income and population began to exhibit unprecedented sustained growth. In the two centuries following 1800, the world's average per capita income increased over 10-fold, while the world's population increased over 6-fold.

The transition began in the later part of the 18th century in parts of Great Britain's previously manual labour and draft-animal-based economy towards machine-based manufacturing. It started with the mechanisation of the textile industries, the development of iron-making techniques and the increased use of refined coal. Trade expansion was enabled by the introduction of canals, improved roads and railways.

The introduction of steam power fueled primarily by coal, wider utilisation of water wheels and powered machinery (mainly in textile manufacturing) underpinned the dramatic increases in production capacity. The development of all-metal machine tools in the first two decades of the 19th century facilitated the manufacture of more production machines for manufacturing in other industries. The effects spread throughout Western Europe and North America during the 19th century, eventually affecting most of the world, a process that continues as industrialisation.

The first Industrial Revolution, which began in the 18th century (about 1780), merged into the Second Industrial Revolution around 1850, when technological and economic progress gained momentum with the development of steam-powered ships, railways and later in the 19th century with the internal combustion engine and electrical power generation (Beck, 1999).

Thereafter, man's dependence upon energy derived from fuel combustion has increased dramatically, the environmental significance of the reactions and products of the combustion of liquid fuels notwithstanding. Petrochemical processes, their products, utilization and the resulting wastes affect life adversely. "Oil spillage, exhaust from motor vehicles, pesticides, fertilizers and acid rain have made our environment unclean and endangered plant and animal life. Human health is also being threatened by environmental pollution" (Ababio, 2005). Understanding the pollutants chemical reactions and products and their environmental, health and socio-economic significance and implications for development would help to forge a way forward.

This review study examines the chemical reactions and the environmental significance of the products of combustion of liquid petroleum fuels, as well as forges the way forward in terms of measures to contain the pollution and corrosion effects and alternative energy sources. After this brief introduction, the rest of the paper is structured as follows: typical properties of common liquid petroleum fuels; polluter reactions and products of liquid petroleum fuels combustion; environmental, health and socio-economic significance and implications for development, way forward and conclusion.

TYPICAL PROPERTIES OF COMMON LIQUID PETROLEUM FUELS

Typical properties of common liquid petroleum fuels have been given (Tedder *et al*., 1975). The specific gravities at 15.5°C are 0.75, 0.78, 0.84 and 0.96 for gasoline, kerosine, gas oil and fuel oil, respectively. The boiling ranges are 30-180, 150-260, 180-350 and 180>370°C respectively. The weight percentage sulphur contents are respectively <0.1, 0.1, 0.6 and 2.5. The calorific values in kilojoule per kilogramme are respectively 47300, 46500, 45600 and 43900. The weight-weight stoichiometric air-fuel requirement is same, 14.7:1, for gasoline, kerosine and gas oil, but 14:1 for fuel oil.

COMBUSTION OF LIQUID PETROLEUM FUELS

Polluter reactions and products A large percentage of all anthropogenic air pollution arises from the combustion of fossil fuels (coal, petroleum oil and gas) (Eneh, 2011a,b; Nwaichi and Uzazobona, 2011). The eight classes of environmental pollutants are oxides of carbon, sulphur and nitrogen, volatile organic compounds, suspended particulate matter, photochemical oxidants, radioactive substances and hazardous air pollutants. Oxides of carbon include carbon(II) oxide or carbon monoxide (CO) and carbon(IV) oxide or carbon dioxide (CO_2) (University of California College Prep, 2009; Eneh, 2011c).

Of particular interest here are oxides of carbon, sulphur and nitrogen. Carbon monoxide is mainly produced by the incomplete combustion of fossil fuels.

$$C_3H_8+3\frac{1}{2}2O=3CO+4H_2O$$

The colourless and odourless gas is also present in cigarette smoke (Alan *et al*., 2003; Stone *et al*., 2001). Carbon dioxide is produced by the complete combustion of fossil fuels.

$$C_3H_8+5O_2=3CO_2+4H_2O$$

Oxides of sulphur include sulphur (IV) oxide or sulphur dioxide (SO_2) and sulphur(VI) oxide or sulphur trioxide (SO_3). Petroleum has sulphur-containing compounds, including thiols (mercaptans), such as ethanethiol (C_2H_5SH) and cyclic sulphides, such as the thiophen derivatives (e.g tetrahydrothiophen and benzothiophen).

Thiols (thio alcohols or mercaptans) are organic compounds that contain the-SH group, called thiol group or mercapto group or sulphydryl group. They are analogues of alcohols in which the oxygen atom is replaced by a sulphur atom. They are named according to the parent hydrocarbon, e.g. ethanethiol (C_2H_5SH), which is an analogue of ethyl alcohol (C_2H_5OH) (Daintith, 2000).

Sulphur oxides are primarily produced by the combustion of coal and petroleum fuels. On combustion, most of the sulphur in petroleum fuel is oxidized to SO_2 and at the most 3% of this is further oxidized to SO_3.

$$S+O_2=SO_2$$

$$SO_2+\frac{1}{2}O_2=SO_3$$

Petroleum contains nitrogen in complex ring structure, such as carbozole (Eneh, 2011a). On combustion of petroleum fuel, the nitrogen is oxidized to oxides of nitrogen, which include nitrogen(II) oxide or nitric oxide (NO), nitrogen(IV) oxide or nitrogen dioxide (NO_2) and nitrogen(I) oxide or nitrous oxide (N_2O):

$$N_2+O_2=2NO$$

$$N_2+2O_2=2NO_2$$

$$N_2+\frac{1}{2}O_2=N_2O$$

Nitric oxide is a clear, colourless gas formed during the combustion of fossil fuels. Nitrogen dioxide also forms when nitric oxide from fuel combustion reacts with atmospheric oxygen.

$$4NO+2O_2=4NO_2$$

ENVIRONMENTAL, HEALTH AND SOCIO-ECONOMIC SIGNIFICANCE AND IMPLICATIONS FOR DEVELOPMENT

The liquid petroleum fuels combustion reactions and products have serious environmental significance and implications for development.

Carbon monoxide: Carbon monoxide is a primary pollutant. It is poisonous to air-breathing animals. With 250 times affinity for haemoglobin than the affinity of oxygen for haemoglobin, it displaces oxygen from haemoglobin, impeding delivery of oxygen to cells.

$$\text{Oxy-Haemoglobin}+CO=CO\text{-Haemoglobin}+\text{Oxy}$$

This causes dizziness, nausea, drowsiness and headaches; at high concentrations it can cause death (Eneh, 2011d).

High concentrations of CO in cities, where automobiles operate at high density, mean that the human heart has to work harder to make up for the oxygen displaced from the blood's haemoglobin by CO. This extra stress appears to reveal itself through increased incidence of complaints among people with heart problems.

Carbon dioxide: Carbon dioxide is considered a greenhouse gas because it heats up the atmosphere by absorbing infrared radiation. As a result of this characteristic, excess amounts of carbon dioxide in the atmosphere may contribute to global warming. Carbon dioxide can also react with water in the atmosphere to produce carbonic acid, H_2CO_3, which dissociates to HCO_3^- that combines with rain water to produce slightly acidic rain.

$$H_2O+O_2 \leftrightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

The sheer quantity of CO_2 emitted in combustion processes of liquid petroleum fuels is increasing the concentration of CO_2 in the atmosphere and enhancing the greenhouse effect.

Thiols: A characteristic property of thiols is their strong disagreeable odour, e.g. the odour of garlic, which is produced by ethanethiol. Unlike alcohols, they are acidic and react with alkalis and certain metals to form salt-like compounds. The older name, mercaptan, derived from their ability to react with mercury (Daintith, 2000).

Oxides of sulphur: Oxides of sulphur have a characteristic rotten egg odour and inhalation of them can lead to respiratory system damage. They react with atmospheric water to produce sulphuric acid, H_2SO_4, which precipitates as acid rain or acid fog.

$$SO_2+H_2O \leftrightarrow H_2SO_3$$

$$H_2SO_3+H_2O \leftrightarrow H_2SO_4$$

$$SO_3+H_2O \leftrightarrow H_2SO_4$$

Acid rain is a secondary pollutant that acidifies lakes and streams, rendering the water unfit for aquatic life. It condenses on metal surfaces, causing severe corrosion when the metal surface temperature falls below 120°C. Acid rain also dissolves limestone and marble structures. It is now widely observed throughout the world (Asmara and Ismail, 2011).

The acid gases, particularly SO_2, increase the rate of destruction of building materials. This is most noticeable with calcareous stones, which are the predominant building materials of many important historic structures. Metals also suffer from atmospheric acidity. In today's photochemical smog, natural rubbers crack and deteriorate rapidly.

Oxides of nitrogen: There has been particular concern with regards to the generation of nitrogen oxides by sources, such as petroleum gas stoves. Nitrous oxide or dinitrogen oxide, N_2O, is a greenhouse gas. Nitrogen dioxide, a reddish-brown pungent gas, is considered to be a secondary pollutant. Exposure to oxides of nitrogen can cause lung damage, aggravate asthma and bronchitis and increase susceptibility to the flu and colds. Nitrogen dioxide, NO_2, can combine with atmospheric water to form nitric acid, which is precipitated as acid rain.

$$2NO_2+2H_2O=2HNO_3+H_2$$

Nitrogen dioxide is also a key ingredient in the formation of photochemical smog. The polluted urban atmosphere contains about 100 different hydrocarbons, the most reactive of which are the olefins. The result of atomic oxygen attack on olefins is production of free radicals. The hydrocarbon radical, RO., reacts with NO_2 to form organic nitrate, RNO_3 or peroxoacyl nitrate (PAN), $R(CO)O_2NO_2$, as follows:

$$RO.+NO_2=RNO_3$$

$$R(CO)O_2.+NO_2=R(CO)O_2NO_2$$

The peroxoacyl radical, $R(CO)O_2.$, is formed by the reaction of free radical, RCO. and atmospheric oxygen:

$$RCO.+O_2=R(CO)O_2.$$

The best known PAN is peroxoacetylnitrate, ($CH_3C.OO.NO_2$) (Spedding, 1974).

PANs are very important in photochemical smog because of their considerable biological activity. The eye irritation caused by the secondary pollutant (PAN) is one of the most characteristic direct effects of the smog. They cause plant leaf damage at very low concentrations and cause eye and respiratory irritation in humans at concentrations as low as 0.5 mg kg^{-1}.

Knocking fuel: Sharma (2002) and Arene and Kitwood (1979) report that poor quality fuel tends to ‘knock’ (explode unevenly and prematurely, especially in a high-combustion engine). Adding small proportions of tetramethyl-lead(IV), $Pb(C_2H_5)_4$, greatly improves the quality of fuel, but leads to environmental pollution and lead poisoning. Lead, from automotive exhausts, is thought by many to be a factor in lowering the IQs of urban children.

THE WAY FORWARD

There are both panaceal and radical change approaches to addressing the environmental challenges of the combustion products of liquid petroleum fuels. The panaceal approach does not address the root causes of the environmental challenges, but are mere measures to contain them. These measures can only minimise the challenges. On the other hand, the radical change approach advocates doing away with fossil fuels and taking to renewable energy sources.

Panacea: Carbon monoxide pollution from automobiles can be reduced through the use of catalytic converters and oxygenated fuels (Eneh, 2011c, d).

Carbon dioxide emissions can be reduced by limiting the amount of fossil fuels burned. More importantly, promoting green environment will enhance the absorption from the environment of CO_2 by plants for photosynthesis -a chemical process by which green plants synthesize organic compounds from carbon dioxide and water in the presence of sunlight.

$$CO_2+H_2O\rightarrow[CH_2O]+H_2O+O_2$$

It occurs in the chloroplasts (most of which are in the leaves) (Alan *et al*., 2003).

Oxides of sulphur can be removed from industrial smokestack gases by scrubbing the emissions, by electrostatically precipitating the sulphur, by filtration, or by combining them with water, thereby producing sulphuric acid which can be used commercially (Eneh, 2011a).

Automobile emissions of these pollutants (NO, NO_2 and N_2O) can be reduced by catalytic converters which convert them to molecular nitrogen and oxygen (University of California College Prep, 2009; Eneh, 2011b).

The use of tetramethyl-lead(IV), $Pb(C_2H_5)_4$, to improve the quality of fuel, which leads to environmental pollution and lead poisoning, should be discouraged. Indeed, it has been outlawed in most countries (Kymisis and Hadjistavrou, 2008; Goss *et al*., 2004; Kim and AAPCEH, 2004). Branched-chain hydrocarbons or aromatic compounds, ethyl alcohol and methyl alcohol have been used to improve the quality of fuels.

Many industries, especially the electronics industry, must take great care over the purity of air where a speck of dust can destroy a microchip or low concentrations of air pollutants change the composition of surface films in component design. Museums must care for objects over long periods of time, so precautions must be taken to protect delicate dyes from the effects of photochemical smog, paper and books from sulfur dioxide and metals from sulfide gases.

Alternative energy sources: The radical change approach is abandoning the environmentally unsustainable fossil fuels-coal, natural gas and petroleum oil-for the alternative renewable energy sources, which include wood and other biomass, hydro, solar, wind, wave, tidal, geothermal, nuclear (fission and fussion), etc. It is heart-warming that no less than 20% of Denmark's energy needs are met by electricity generated by wind turbines. Other alternative energy sources deployed by the country include the burning of waste products or biomass in combined heat and power plants, electricity generated by escape of photovoltaic or solar energy cells and geothermal turbines powered by the escape of underground steam. Indeed, alternative energy technologies and conservation of energy are watch-words for the average Dane and the country generates its highest proportion of electricity by renewable energy sources (Isife, 2010).

CONCLUSION

Man's activities have generated so much polluters for the air, soil and water environments, thereby threatening human health and endangering plant and animal lives. Since the time of the Industrial Revolution, there is dramatic increase in human dependence on energy derived from the combustion of petroleum fuels. Yet, environmental pollution arising therefrom is posing some serious environmental challenges.

The study has attempted to review the chemical reactions procuring environmental pollution and corrosion derivable from the combustion of liquid petroleum fuels, particularly the oxides of carbon, sulphur and nitrogen. How to minimize the challenges posed by these environmentally significant combustion products of liquid petroleum fuels were also examined under panaceal and radical change approaches. The former suggests remedial measures, while the latter advocates radical change from fossil fuels to renewable energy sources, giving Denmark as an example of success story.

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