

ENVIRONMENTAL CHEMICAL PROCESSES: PROBLEMS AND PROSPECTS

R. B. SALAU

Chemistry Department, Federal University of Technology
P.M.B 65 Minna, Nigeria
rasaqbsalau@yahoo.com

Abstract

Environment is an archive of various processes and interactions which naturally ought to be in equilibrium. However, unmitigated activity of some of these processes could shift these expected equilibrium positions. This paper x-rayed some chemical reactions of the environment with particular emphasis on those reactions that portend serious threat to the natural ecological balance. Problems emanating from ecologic cycles obstruction by natural or anthropogenic influences were mentioned. This includes fossil fuel burning, gas flaring, large scale deforestation, desert encroachment, global warming, acid rain, urban water pollution, automobile emissions, ozone layer depletion and other related problems. It further suggests measures ranging from mitigational control to impetus for the emergence of the green chemistry concept required to moderate environmental hazards right at source. This concept is a especially valuable in real time analysis to prevent pollution and designing chemicals, product and reaction conditions that will ultimately lead to a minimized environmental hazards.

Key words: Environment, harzard, ecological balance, mitigational ontrol, green chemistry.

INTRODUCTION

Environment is a natural world of living and non living things and the global scheme of the water, air and soil. Environment is a multi disciplinary concept as its perspective cuts across all fields of human learning.

Reactions of physiochemical interactions of the environment component fall within a brand of environmental perspective called environmental chemistry. More technically, the environmental chemistry encompasses the study of the sources, reactions, transport, effects and fates of chemical species in the air, soil and water scheme of the environment as well as the effect of human activities. The influence environmental chemists are therefore concerned with the study of chemical and biochemical phenomena that occur in the environment. Environmental chemists' approaches include: mapping out of the concepts of chemical reactions, equations, solutions, units sampling and analytical techniques towards explaining the earlier mentioned phenomena in the environment.

The environmental chemist also studies the chemical basis of various ecologic cycles in a natural state as well as to qualifying, quantifying and presenting the extent of human influence on the activities on these natural cycles. Thus, reactions to be observed can be normal or adverse. Reactions become adverse if the product obtained has detrimental impact on the environment. These products are called pollutants or contaminants of the environment. These products usually have adverse effect on the receptor medium or organism and the retaining sinks.

This paper is at reviewing some reactions of the

ecological cycle in the environment, identifying some hazard - proned ones and discussing some control measures.

CHEMICAL COMPONENTS OF THE ENVIRONMENT

The earth environment consists of three interactive sectors which are the lithosphere (earth crust), hydrosphere (water part) and the atmosphere (air part). The earth crust of many chemical elements out of which the following occur in significant quantity in the order: oxygen (46.6%), silicon (27.7%), aluminum (8.1%), iron (5.0%), calcium (3.6%), sodium (2.8%), potassium (2.6%), magnesium (2.1%), others (1.4%) (Raiswell, 1992). These elements occur as ore-a natural combined state in which elements exist. They are mostly in the form of oxides and that's why oxygen ranks very high as the chief component earth crust.

The hydrosphere is a collective term for various forms of water-oceans, seas, lakes, rivers, ground water or glacier etc. the ocean occupying 70% of the earth surface. It is therefore a major player in the physio-chemical shaping of the earth as well as climatic changes. The ocean absorbs radiation and distributes it round the world. It also regulates the proportions of the life molecules: oxygen and carbon (iv) oxide. Major chemical elements are hydrogen, oxygen, carbon, dissolved elements and combined elements of chlorine, Sulphur, sodium, potassium, magnesium etc. The atmosphere consists mainly of elements Nitrogen (78%), Oxygen (21%), Argon (0.9%) and Carbon iv oxide (0.03%) together with varied proportion of water vapour.

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INTER AND INTRA SECTORAL INTERACTIONS IN THE ENVIRONMENT

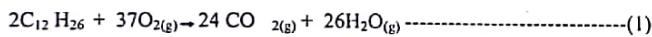
The environmental sectors lithography, hydrosphere and atmosphere work together in a manner analogous to a chemical engineering factory. This processing plant is referred to as earth-air-water factory (Garrels and Mackenzie, 1971). The chemical processes in the factory include the terrestrial, atmospheric reaction and oceanic chemical reactions. Energy used to fuel the chemical process includes solar radiation, mechanical energy, chemical energy and the earth's heat energy.

ECOLOGICAL REACTION CYCLES

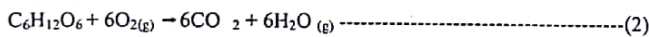
Ecological chemical reactions are the results of interaction among various living things and their physical and chemical environment. In this interaction process, certain common chemical substances are kept fairly constant, except or otherwise disrupted either by direct human activities or over use or non use of some reaction products. Some of the natural compounds of environmental significance include: oxygen, water, carbon iv oxide and nitrogen. The studies of their cycles are very crucial to the ecological balance of the environment.

OXYGEN CYCLE

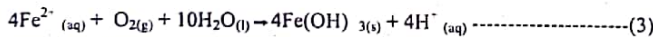
Oxygen is consumed in the form of burning or oxidation of organic matter like oil, coal and other contained in ancient sedimentary rocks. Modern organic materials burning also consume oxygen or as oxidative decay of vegetation in soil and even in respiration process. In geological exploration, oxidation of reduced inorganic species also takes place such as iron (II) bearing mineral exposed by erosion and reduced gasses from volcanic activity.



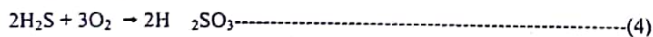
Pure gasoline



Simple food

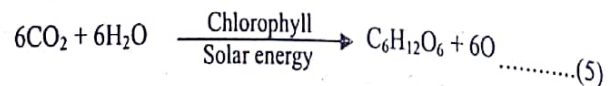


Iron ion in silicate



Volcanic gas

The major way of returning oxygen to atmosphere is through photosynthesis. Photosynthesis is a process of synthesizing food by terrestrial and marine green plants



makes use of water and in the end brings back oxygen to the atmosphere.

Problem of oxygen cycle

Residence time of atmospheric oxygen is given as 7600 years (Garrels and Mackenzie, 1971) implying that large consumption of oxygen ought not to significant effect in depleting oxygen reservoir. It has also been used to determine spatial variability of atmosphere gasses on a global scale. Residence time is also interpreted; in this case, to represent the minimum time O₂ reservoir can be exhausted assuming there is constant recuperation through photosynthesis. However man's activity has betrayed this expectation. Processes such as the burning of fossil fuel, large scale deforestation, destruction of vegetation for building and desert encroachment have had direct bearing on the depletion of the reservoir of oxygen. Obstruction of the Photosynthetic process by anthropogenic influence therefore constitutes a potential calamity. The envisaged problem is more of starvation which is triggered off than the inadequacy of oxygen that also results. In either case, man is at the receiving end. Oceanic and terrestrial reservoirs of oxygen are much more affected by the depletion. This spells doom to living organism inhabitants.

CARBON (IV) OXIDE CYCLE

The carbon (IV) oxide gas is introduced to atmosphere by respiration and other forms of combustion of carbon, organic materials and fossil materials such as coal and petroleum. It is withdrawn from the atmosphere through the process of photosynthesis. The exchange of carbon (IV) oxide gas within the environment is mainly through degassing or dissolution. This is done between water and atmospheric environment. Similarly, the additional carbon (IV) oxide balance is a difference between the atmosphere, where it is formed and also released to and the biosphere environment, where it is released.

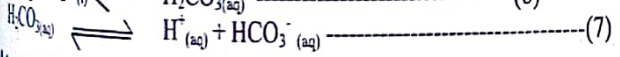
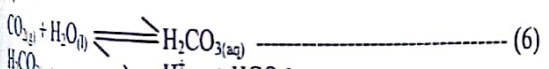
Problem of carbon (IV) oxide cycle

The residence time of the carbon dioxide is put around 20 years. Low residence time is low indicating that there is rapid depletion of its reservoir (Woodwell, 1978). Man's activities over time introduce a reservoir which increases the amount of carbon (IV) oxide present in the atmosphere. This is by burning of fossils fuels and other reactions which emit carbon (IV) oxide. The result is that much more than of carbon (IV) oxide than will cause comfort is present. This, of course, has climatic

application. Radiations from solar energy are trapped in water vapour, ozone and carbon (IV) oxide. Carbon (IV) oxide absorbs radiation at longer wavelength. The heat reflected from the earth's surface is at longer wavelength than their incoming solar radiation because the earth's surface temperature is cooler. This reflected heat is absorbed by carbon (IV) oxide and the partly re-radiated back to the surface. The earth's atmosphere becomes warmer since less heat is re-radiated to the outer space. This is the green house effect. The problem at hand therefore is the global warming. The carbon (IV) oxide present in the atmosphere, therefore, is said to be at pollution level.

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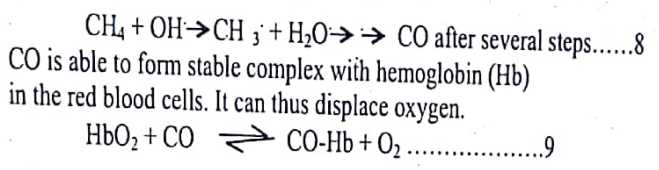
Presence of dissolved carbon (IV) oxide gas is $CO_{2(aq)}$ is a more abundant. However the dissolved carbon (IV) oxide practically exists as in the formula H_2CO_3 . This is carbonic acid. It is formed as rain washes down the gas. This is an acid rain situation.



At equilibrium, continuous addition of $CO_{2(g)}$, shifts equilibrium position to the formation of carbonic acid, which further splits to introduce acid (H^+ ion). The pH becomes lower indicating acidity. This acid solution, in this case, is a weathering agent. Further carbon (IV) oxide gas is produced by oxidation of plant and animal and the oxidation of organic matter by microorganism. The result is that soil water is made more acidic and could constitute an ecological danger.

Other forms of carbon whose presence in the environment has a detrimental effect on the environment are carbon (II) oxide and soot which is purely elemental carbon. The carbon (II) oxide adverse effect on human being is through interference with oxygen transport in the body. In the urban area, both carbon (II) oxide and soot arises from incomplete burning of substances especially fuel. They are found as component of exhaust fumes of vehicle or industry. The soot constitutes aerosol burden in urban and sub-urban. In non-urban atmosphere, 80% of

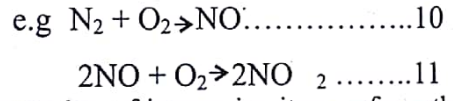
Carbon (II) oxide is sourced from methane produced by the microbial decomposition of living matter REF. The methane reacts with hydroxyl radicals, further steps lead to production of carbon (II) oxide.



NITROGEN CYCLE

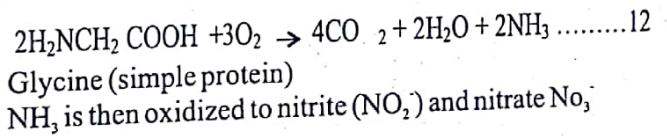
The reaction processes involved in the nitrogen cycle within the earth atmosphere and water cycle within the environment: hence the equilibrium presence of nitrogen is maintained constantly by the process described below:

Combustion and effect of lightening on nitrogen (N_2) or nitrogen I oxide (N_2O) leading to discharge of ammonia (NH_3), ammonium (NH_4^+) and nitrogen (IV) oxide (NO_2). This reaction occurs within the atmosphere

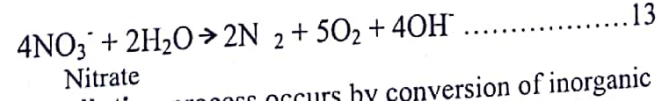


Evaporation of inorganic nitrogen from the earth crust form the product of reaction 9 above. There is also precipitation process for the product of reaction 9 from inorganic nitrogen in the earth crust or ocean.

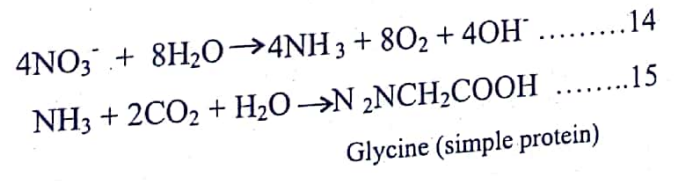
Mineralization process occurs by conversion of organic nitrogen in both earth and ocean to form inorganic nitrogen.



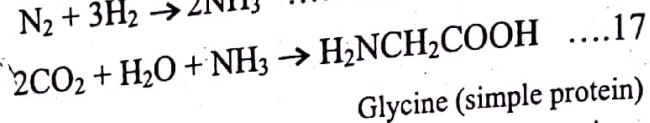
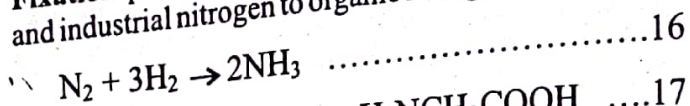
Dentrification process occurs by converting inorganic nitrogen of the earth or ocean to atmospheric nitrogen.



Assimilation process occurs by conversion of inorganic nitrogen of the earth and ocean to organic nitrogen.



Fixation process occurs by conversion of atmospheric and industrial nitrogen to organic nitrogen.



Glycine (simple protein)

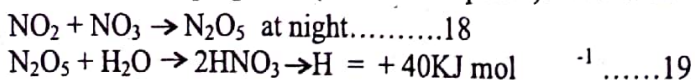
Problem of nitrogen processes lies in the disruption of equilibrium condition existing between the natural the inorganic nitrogen reservoir (Liu, *et al* 1977) and the introduction of fertilizer nitrogen aided by precipitation of fossil fuel burning. Similarly, the excessive run-off of nitrogen into the streams or lakes rapidly increases the population of algae who subsequently, deplete other important nutrient like phosphorus in the water environment. These algae themselves die and the decay of their cell materials through aerobic process reduces the oxygen content of water leading to eutrophication condition whereby fish and other oxygen dependent organism are destroyed.

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Pollution of the atmosphere can arise from the presence of some oxides of Nitrogen (NOx) and compounds of nitrogen such as nitrogen (II) oxide (NO), nitrogen iv oxide, nitrogen (IV) oxide, nitrogen (V) oxide N₂O₅, nitrous acid (HNO₂) and nitric acid (HNO₃). The role of NOx as photochemical smog precursor and in the formation of peroxy acyl nitrate (PAN) which are very toxic to plant as well as causing oxidative damage to fabrics, plastics and rubber.

Nitrate polluted of drinking water is possible when nitrate is in large amount. It is reduced to nitrite in stomach leading to the disease known as *methaemoglobinaemia*. This situation often lead to sickness or death in human and ruminant especially in plants.

Presence of oxide in the atmosphere can lead to acid rain or acid leach by atmospheric water vapour. Combination of nitrogen (IV) oxide and nitrogen (VI) oxide to form nitrogen (V) oxide at night is also a precursor reaction for formation of tropospheric (lower atmosphere) nitric acid.



SULPHUR CYCLE

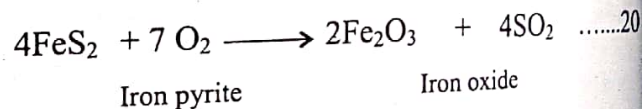
Sulphur element is introduced to the environment naturally. Man's activities had over the time, added more

artificially. The atmospheric form of sulphur is obtained as sulphur (IV) oxide (SO₂) gas and hydrogen sulphide (H₂S) gas, whereas the hydrospheric and lithospheric form of sulphur exists as acid and in complex organic content like coal, vegetation, crude oil etc.

Actions of anaerobic bacteria in solution marshes lead to the release of hydrogen sulphide (H₂S) gas and SO₂ gas to the atmosphere from the earth. The sulphur is returned by oxidation of SO₂ to SO₃, washing down of SO₃ by water droplet or rain as acid back to earth or ocean, interaction of the acid with some salts convert the sulphur to sulphates. The oceans are the main sink for S-compounds.

Naturally, H₂S is produced by aerobic bacillus bacteria, sea sprays like in the case of beach breeze which produce salty particulate sulphate. Volcanoes release both SO₂ and H₂S.

Man's activities have also increased the emission of sulphur oxides to the atmosphere through combustion of fossil fuel, coal, wood, petrol etc. automobile exhaust, electric power generator. Sulphur is in the form of mineral iron pyrites in coal which is oxidized at high temperature.

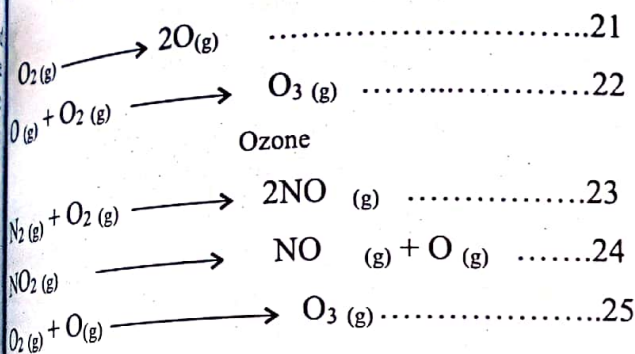


Problems of sulphur cycle

Sulphur IV oxide is probably most dangerous atmospheric pollutant being one of the major constituent of photochemical smog. History was made in December, 1952 (Wilkins, 1954), when a fatal smog occurred, aggravated by extended temperature inversion leaving 12, 000 people dead in two months due to severe respiratory ailment. Photochemical smog is a complex meteorological phenomenon which is an accumulation of various gaseous and particulate pollutants. The SO₂ pollutants in the smog cause respiratory irritation as well as obscure visibility. Also eye irritation is generally caused by photochemical smog. Other constituents of photochemical smog are ozone, oxides of nitrogen, ammonia, soot, methane, aldehyde, peroxy acyl nitrate (PAN) etc.

OZONE CYCLE

Ozone (O₃) is an important constituent of stratosphere layer of the atmosphere. Ozone formation at this layer is initiated by photo dissociation of oxygen molecules by high energy ultraviolet rays. The ozone is converted back to oxygen by reaction with nitrogen II oxide formed by lightning. The ozone cycle is summarized thus:



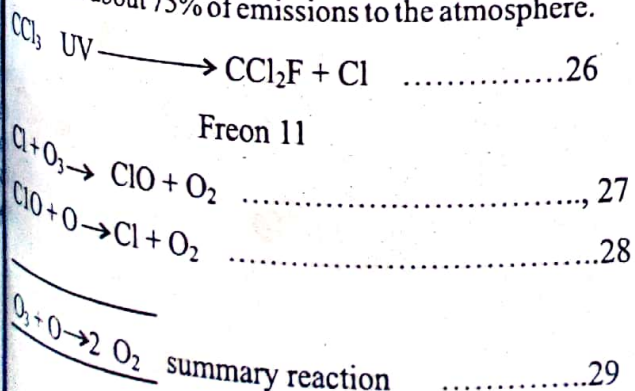
This is equilibrium balance of ozone as a layer in the atmosphere between its dissociation by NO and formation through oxygen molecules. The ozone layer has been doing the shielding of the earth from intense ultraviolet radiation from the sun.

Problems of Ozone cycle

Firstly any thing that hinders the availability of oxygen molecules in the stratosphere may count on the ozone balance. However, giving that the oxygen molecule is constantly available, human activities have contributed tremendously in depleting the ozone balance in the atmosphere (Liu, *et al* 1977). The hazards involved therefore are the exposure to ultraviolet radiation which affects the eye causing keratoconjunctivities (cornea infection), skin reddening (erythema), and skin cancer. Others are changes in visual parameter, acute respiratory and cardiovascular diseases among others.

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In the depletion of ozone layers, chlorofluorocarbon or CFC has been implicated. The CFC includes: Freons Cl_2CF (Freon-II) and Cl_2CF_2 (Freon 12). They are man-made chemicals used as refrigerants and propellants in aerosol spray can. The use especially as propellant account for about 75% of emissions to the atmosphere.



CONTROL OF HAZARDS OF ECOLOGICAL CYCLES

The deviation from equilibrium of the processes in the ecological cycles mostly arises from intervention of human activities. Most of the activities are unavoidable and sometimes irreversible. The predisposing factors are their anthropogenic or natural control options are therefore those of mitigation or minimization. These controls are often backed with legislation or conference resolutions.

The fear of depletion of oxygen depletion are often allayed by encouraging the flourishing of green plants and hence photosynthesis to return oxygen to the environment. The oceanic oxygen depletion due to high consumption of dissolve oxygen is also remedied by reducing the amount of land-derived nutrients reaching the rivers or ocean in runoff. This is achieved by improving sewage treatment and reducing the amount of fertilizers leaching into rivers.

Global warming due to the rising level of carbon (IV) oxide in the atmosphere is tackled at a technological level such that there is an efficient mixing mechanism where ocean is able to take up the gas then precipitating it as limestone and the design of a booster device for increased plant growth (Bajah *et al*, 1992). Also there had been a developed renewable energy standard equipment to mitigate global warming (Woodwell, 1978).

In the recent time particulate filter technologies have been employed to serve as highly effective means of eliminating particulate matter or soot particularly from diesel exhaust. The accumulation of carbon (II) oxide in the atmosphere is tackled by controlling the exposure sources, observing strict personal hygiene procedure and use of personal protective equipment and storage designs.

Controlling acid rain taken the form of use of market incentives. In U.S for instance, the congress established the acid rain program under the 1990 clean air amendment. This called for major reduction in the sale of electric generating facilities emitting sulphur (IV) oxide SO_2 and oxides of Nitrogen NO_x . These are the common components of acid rain.

Nitrate pollution of river water can be controlled through the policies of restriction of river flow in the some marked areas. These measures were found to reduce nitrogen pollution (Istvan *et al*, 1991).

Photochemical smog can be controlled through policies which are technologically inclined such that both hydrocarbons (HC) and oxides of nitrogen NO_x are monitored and controlled. This device employed the installation of positive crankcase ventilation (PVC)

technique on used and new cars to control the major sources of HC and NO_x. The second control step was to establish exhaust emission standards for HC and CO (Pitts J.N.J 1997).

Legislations like ban of CFC aerosol propellants have been enforced in countries like Canada and United States of America as early as 1978. Montreal protocol as amended in 1990 pledged to stop all CFC production by year 2000. Technologically, installation of recovering and recycling units for CFCs from used refrigeration systems and motor vehicle air conditions became an important practice to control the venting of the CFCs into the atmosphere. In addition, use of substitutes for CFC have been developed and in use. These alternatives that have low ozone depletion potential (ODP) refrigerant, aerosol propellant and solvents include hydrochlorofluorocarbons (HCFCs) e.g. CF₃CHCl₂, hydrofluorocarbon (HFCs) e.g. CF₃CH₂F, hydrocarbons (HCs) e.g. butane, propane. The CFCs used as solvent can be replaced with water and steam in cleaning applications (Johnston, 1992).

PROSPECTS FOR A CLEANER ENVIRONMENT

The rising wave of technological advances gives hope that environmental protection is a possibility. When all the controls are strictly applied, the normal ecological order would prevail.

Advances in environmental protection have brought in a new concept of **Green Chemistry**. This newly fashioned sustainable chemistry emerged about a decade ago. It is the design, development and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and environment. While environmental chemistry studies chemical and biochemical phenomena that occur in natural places, Green chemistry seeks to reduce potential pollution at source (Ryoji, 2005).

environment. While environmental chemistry studies chemical and biochemical phenomena that occur in natural places, Green chemistry seeks to reduce potential pollution at source (Ryoji, 2005).

The principles of **green chemistry** are to; prevent waste, design safer chemicals and product, design less hazardous chemical synthesis, use safer solvents and reactions condition, increases energy efficiency, design chemicals and products to degrade after use, analyze in real time to prevent pollution and minimize potential for accident. The **green chemistry** ability to tackle environmental hazard was described (Ryoji N., 2005). This is about the technology of a competing liquid CO₂ cleaning process called dry wash. The thrust is identification of three key developments area using the green chemistry concept: These are the use of supercritical carbon (IV) oxide as green solvent, aqueous hydrogen peroxide for clean oxidation and the use of

hydrogen in asymmetric synthesis. Examples of applied green chemistry are supercritical water oxidation, on water reactions and dry media reactions.

One of the major environment pollution where the concept of green chemistry could be applicable includes gas flaring. A gas flare is a chimney or chimney related design found on oil wells or oil rigs and in refineries, chemical plants and landfills used for burning off unwanted gas (John., 1985. Milton., 2005. David., 2006). Recently, under the Kyoto treaty, some developing countries garbage collecting companies received carbon bonus for installing burning chimneys for the methane gas produced at their land fills, this way that methane reaches the atmosphere. After the burning, this gas is converted to heat, water, and carbon IV oxide and according to the third assessment report of International Governmental panel on climatic change (IPCC), methane is 25 times a more powerful green house gas than carbon IV oxide. Effort to burn methane is towards reducing green house effect.

Green chemistry approach to this is manifested in the recent development of fuel cell in Japan (Tomita et al., 2008). This cell can convert methane to methanol, which is a very useful fuel, at moderate temperatures. By this way, the question of green house effect due to methane is completely ruled out.

Desertification problem can be summed up as the process which converts productive land into non-productive desert, due to poor land management policies. Over the time, attempts were made in curbing over-grazing by legislation and policies. Desertification reduces greatly the ability of land to support life. One of the area of focus of green chemistry is the use of greener synthetic pathway (Paul and John., 1998), introduced greener feed stocks that are innocuous or renewable such as biomass and natural oils. This served as alternative instead of excessive over gazing by animals. that are innocuous or renewable such as biomass and natural oils. This served as alternative instead of excessive over gazing by animals.

Similarly, the problem of deforestation could also be tackled from the green chemistry angle. Deforestation in the real sense is not only conversion of forest to non-forest but also degradation that reduces forest quality, the density and structure of trees, the ecological services supplied, biomass of plants and animals, the species and genetic diversities. Reforestation goal is the ultimate goal of green chemistry. Going by Chinese experience, a deliberate action plan can be made to get tree planted at particular rate; daily, weekly or even plantation holiday.

CONCLUSION

7.0 The environmental spheres: atmosphere, hydrosphere, and lithosphere interaction is analogous to a chemical plant whose functional components are cross-linked. Thus, all ecologic cycles cut across these phases.

The issues arising from obstruction of the natural balance include various ways by which the associated problems could be arrested. The problem which include ozone layer depletions, photochemical smog, nitrate pollution, acid weathering, global warming and green house effect, automobile emissions, desertification, gas flaring and deforestation to mention but few.

Methods of control or mitigation could take the form of studying the pattern by which the problems arise and making plans in opposite direction. Example of this is the massive tree planting policies for deforestation. Accepting the lesser evil of burning the methane gas in landfills chimney to carbon IV oxide. The green house effect of the latter 25 times of less effect than the former.

The green chemistry approach to controlling problems is by redesigning the chemicals, products or reaction conditions to minimize hazards. The example can be found in the conversion of methane to methanol in the chimney of landfills. This is to reduce green house effect arising from both methane and carbon IV oxides. Methanol can therefore, be positively used. Another example of this approach is to synthesize feed stocks as alternative to over-grazing.

The series of actions and reactions, which are essentially natural, and indeed in equilibrium not only needs human intervention for their disruption but also for their corrections. Hence, environmental protections from hazards are possible applying appropriate control measures such as: legislations, policies and technologies.

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