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A review of recent advances and the future of green chemistry in meeting the challenges of sustainability

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Abstract
The quality of life and the very manner of living are dependent on chemical innovations. The chemical enterprise faces a dilemma: how to produce the goods and services on which the society depends in a manner that does not harm the environment. Finding creative ways to protect and improve the air we breathe, the water we drink and the land that sustains us while enhancing human progress is a challenge we must embrace. Green chemistry is playing an ever-increasing role in helping the chemical enterprise rise to these challenges.

Keywords: feedstock, sustainability, renewable resources, benign

Introduction

Green Chemistry is defined as invention, design, development and application of chemical products and processes to reduce or to eliminate the use and generation of substances hazardous to human health and environment (Anastas and Warner., 1998) [1]. Recent advances in green chemistry have attempted to address both obvious hazards and those associated with global issues such as climate change, renewable energy sources, availability of potable and adequate fresh water supply, waste generation and disposal and adequate food production to meet the ever increasing world population. The major trust of green chemistry is a responsible care of the environment through research, education, industrial implementation and government intervention by way of proper and prompt legislation.

Broadly speaking, the procedures in the design of environmentally benign products and processes are basically based on twelve sets of principles called the 12 Principles of Green Chemistry. According to Anastas and Kirchhoff (2002) [2], the concept of design in the definition of green chemistry is an essential element in requiring the conscious and deliberate use of a set of criteria, principles and methodologies in the practice of green chemistry. It therefore, addresses hazards, whether physical (flammability, explosivity), toxicological (carcinogenicity, endocrine disruption), or global (ozone depletion, climate change) as an inherent property of a molecule, (Anastas., 2003) [3].

Principles of Green Chemistry

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that posses little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvent s, separation agents *etc*.) should be made unnecessary wherever possible and, innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material feedstock should be renewable rather than depleting whenever technically and economically practical.
8. Unnecessary derivatization (blocking group, protection/de-protection, and temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the forms of the substance used in chemical reaction should be chosen so as to minimize the potential of chemical accidents, including releases, explosions, and fires (Anastas and Warner, 1998) [4].

Researches with excellent results/outcome are being conducted by the incorporation of one or more of the 12 Principle of Green Chemistry. These principles are a categorization of the fundamental approaches taken to achieve the green chemistry goals of benign synthetic route and design criteria by molecular scientists.

In the US, foundation works in chemistry and engineering at the National Science Foundation's programme on Environmentally Benign Syntheses and Processes was launched in 1992 and went into partnership with EPA through an MOU. Thereafter, the name "US Green Chemistry Program" was adopted. Since its inception, it has served as a focal point for major activities within the United

States, such as the Presidential Green Chemistry Challenge Awards and annual Green Chemistry and Engineering Conference (Parent and Kirchhoff, 2014) [3].

he same period, other research hubs around the world (Italy, the UK, Japan, Germany, Australia, etc) initiated their versions and adoption by industries was evident although difficult to quantify. They have also put in place one form or the other of green chemistry awards to highlight the environmental and economic achievement of green chemistry. In Africa, GCI have affiliate chapters in Senegal and South Africa as far back as 2002. In developing countries, the introduction of green chemistry is still at its infancy, despite the significant need and the significant role green chemistry can play. Many of the practices in developing countries are still far from the concepts of safety, pollution prevention, and design of energy efficiency. Sadly, Nigeria is still searching for its feet on this one, (CSN, 2010).

The first green chemistry workshop in Africa was held in Ethiopia, and was jointly organized by the Schools of Chemistry of both Addis Ababa University (AAU) and the University of Nottingham, USA in association with Chemical Society of Ethiopia (CSE). The objectives were firstly to create awareness among academics and professionals in the country, and, secondly to sensitize the policy makers to the role of green chemistry in environmental sustainability. This makes Green Chemistry particularly attractive to the needs of African countries especially those faced with an increasing demand for resources and rapidly expanding populations.

A pan African Green Chemistry workshop was later held in South Africa in 2007. This has resulted in studies of coordination compounds in solvent free medium and ionic liquids thereby avoiding the traditional volatile organic solvents which are considered carcinogenous. In furtherance of this movement, the first workshop on green chemistry in Nigeria was held in 2010 at the chemical Society of Nigeria annual International Conference, Workshop and Exhibition held in Abeokuta Nigeria with Green Chemistry as the major theme. (www.chemsocnigeria.org)

Recent Advances

Research programmes carried out in centers located in these research hubs are focusing efforts around the principles of green chemistry. It is a broad based research programme which encompasses almost all aspects of chemistry. Although the efficiency of a reaction can be measured in many ways, by far the most common method is to calculate the yield. Yield is the universally accepted metric in chemistry research for measuring the efficiency of a chemical synthesis. It provides a simple and understandable way of measuring the success of a synthetic route and of comparing it to others.

Green Chemistry teaches us that yield is not enough. It fails to allow for reagents that have been consumed, solvents and catalysts that will not be fully recovered, and, most importantly, the often laborious and invariably resource- and energy-consuming separation stages such as water quenches, solvent separations, distillations, and recrystallizations. Green Chemistry metrics are now available and commonly are based on “atom efficiency” whereby we seek to maximize the number of atoms introduced into a process into the final product. Synthetic methodologies that are environmentally benign and atom economic are being developed in area of pharmaceuticals. (Trost, 1991).

In the synthesis of Ibuprofen, the traditional method yielded 40% atom economy but in the alternative green methodology an atom economy of 77% was observed. This is a significant improvement especially since it’s a three step synthesis as compared to the multi-step process of the former.

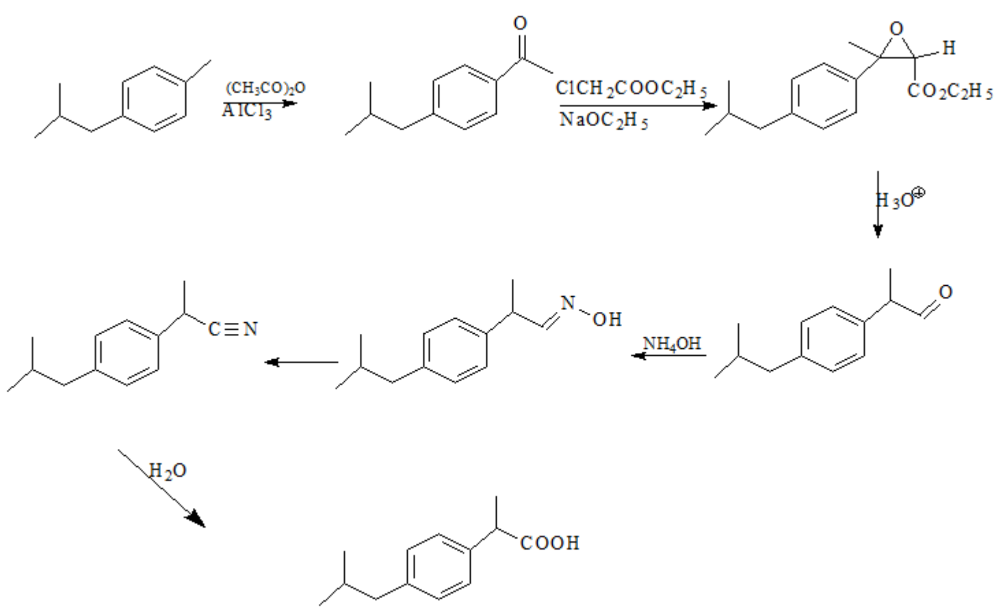

Fig 1: Traditional synthesis of Ibuprofen by Boots.

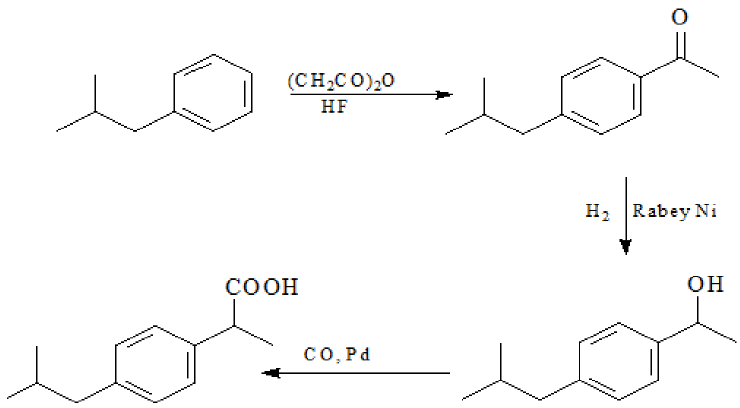

Fig 2: Green alternative synthesis of Ibuprofen by BHC.

Advances have been recorded in the area of agrochemicals. Excellent example of these types of chemicals of less toxicity with high efficacy can be seen in pesticide for controlling insects and marine fouling organisms. The growth of unwanted plants and animals on the surface of a ship costs about $4b a year to combat. Part of this money is needed to overcome what is known as hydrodynamic drag which causes pollution and by extension, global warming and acid rain. With the discovery of a new class of isothiazole compounds, the cost is drastically reduced and the antifoulant developed is safe with no risk to non-target organisms. (www.epa.gov/greenchemistry/aa98b. html).

Many organic reactions utilizes large amount of organic solvents which are toxic. New technologies for the design and application of surfactants for carbon dioxide promises to resolve this dilemma. New efforts and breakthroughs have replaced organic solvents with water, CO_2 and room temperature ionic liquids. The use of supercritical CO_2 as a reaction medium in organic synthesis provides an excellent example of the evolution from the laboratory to the industrial process. Supercritical CO_2 is able to effectively de-caffeinate coffee while eliminating the health and environmental risks associated with the use of methylene chloride, (Parent and Kirchhoff, 2004) [3].

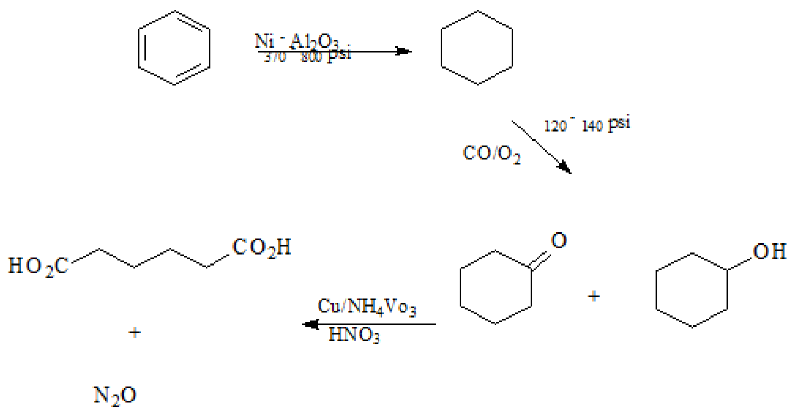

Fig 3: Traditional synthesis of adipic acid using benzene.

Most starting materials on organic synthesis are ultimately derived from crude oil, a depleting finite source. In order to achieve sustainability, researchers and chemical industries needs to focus more on renewable feedstock. The Draths-Frost synthesis of adipic acid and cathechol was developed using bio-catalysis and renewable feedstock to create alternative synthetic route to chemicals of major industrial importance.

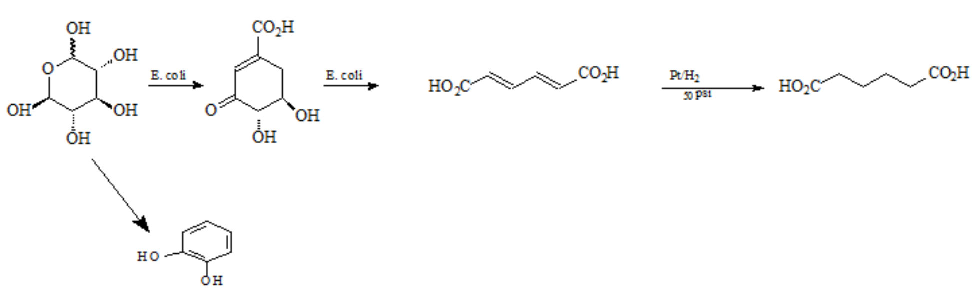

Fig 4: Alternative biosynthetic pathway to adipic acid and catechol, using glucose.

In this process, non-toxic glucose was employed as starting material and water is used as primary solvent. In contrast to the traditional method, this brilliant process avoided the generation of toxic intermediates and environmentally damaging by-products. (Draths and Frost, 1990a,b) [7, 8].
Conversion of waste biomass to animal feeds, chemicals and fuels has gained prominence recently. A family of technologies have been developed that converts waste biomass to animal feeds, industrial chemicals and fuels. They can also be converted to volatile fatty acid salts when fed to anaerobic fermentor. Or concentrated and converted to fuel by acidification or thermally converted to ketones or hydrogenated to alcohols, (Chang *et al*., 1997; Draths and Frost, 1990c,d) [9, 10].

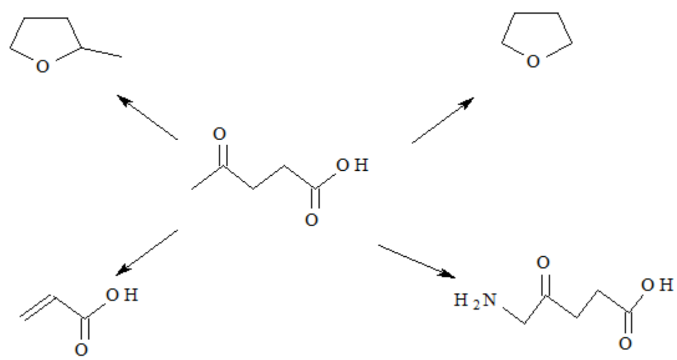

Fig 5: Derivation is minimized and feedstock is renewable.

By producing chemicals from biomass, non-renewable resources such as petroleum and natural gas are conserved for future generations. As we all aware, we do not inherit the earth from our fathers. Rather, we are borrowing it from children (Brower., 2000). Syntheses of pharmaceutical agents are frequently accompanied by generation of a large amount of waste. This is due to the multi-step reactions involved, each of which requires additional feedstocks, reagents, solvents and separation agents. In the discovery and development of an anti-convulsant drug candidate for the treatment of epilepsy and neurodegenerative disorder, *cephalexin*, steps were reduced and yield was better environmentally.

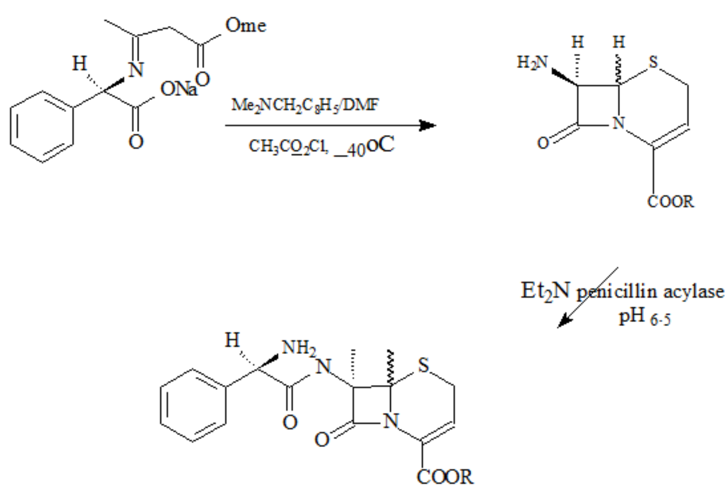

Fig 6: Enzymatic synthesis of Cephalexin.

One of the major problems facing our society is the enormous accumulation of waste in the form of trash. Health and Safety are critical concerns for public health officials, customers and food industry. The design of food packaging materials is very essential and the consideration is to develop materials that protect food and then biodegrade after their useful life is over. Lactic acid obtained from glucose has been found to be biocompatible and are already in use as sutures in medical practices. Currently, McDonalds, a major fast food outlet now uses plastic containers and bags that are biodegradable, a development that's environmentally friendly, (Gross *et al*., 1994; Gross and Kalra, 2002) [11, 12]

Current Challenges

When the world body, United Nations Educational Scientific and Cultural Organization (UNESCO) declared 2005-2015 as the world decade of education for sustainable development, it was in the believe that sustainable development will be integrated into the policy trust of nations around the world. Sustainable development is often defined as "the development that meets the needs of the present, without compromising the ability of future generations to meet their own needs" (Parent and Kirchhoff, 2004) [3].
In a world with a continuously increasing population and limited resources, the idea of a sustainable development is of major

importance as it is for the future. Only research and innovation will allow the development of economic and social networks and processes that fulfill the requirements of sustainability. Sustainability, in science and technology, begins when we start thinking of how to solve a problem or how to turn science into technology. Chemistry, as the central science, plays a central role in this process. It is the bridge between physics, material sciences, and life sciences.

The foremost challenge to sustainability is the ever increasing world population. Human population growth is at the root of virtually all of the world's environmental problems. Although the growth rate of the world's population has slowed slightly since the 1990s, the world's population increases by about 77 million human beings each year. As the number of people increases, crowding generates pollution, destroys more habitats, and uses up additional natural resources, (UN, 1998).

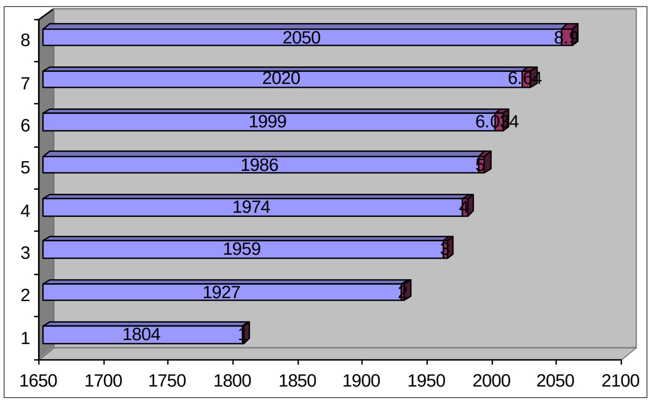

Fig 7: World Population projection, 1998.

The current global population of over 7 billion is already two to three times higher than the sustainable level. With this increasing population comes a demand for resources. One illustration of this is what is currently happening to fresh water aquifers all around the world. Over half of the world population lives in countries where aquifers are being over pumped. As "fossil" aquifers are pumped, the water is not replaced and when that water is depleted, pumping ends since there is no more water flowing in.

When this scenario happens, the tendency is to resort to non-fossil aquifers. But non-fossil aquifers have a recharge rate – the rate at which new, fresh water flows in. As long as water is taken out at or below the recharge rate, the aquifer will continue to supply the same amount of water all year round, year after year. However, these rechargeable aquifers are being over pumped due to population explosion and when aquifer reserves are depleted and fall back to the recharge rate, millions of people suffer and by extension other resources decline as well.

Less than 1% of the Earth's water is fit and available for human consumption due in part to inefficient use, degradation by pollution and of course the unsustainable use of the underground water in aquifers. About a billion people live in countries with absolute water scarcity and most of this population is in overpopulated, fast-urbanizing countries of Asia, Latin America and Africa with polluted rivers and wells that are carriers of disease bearing germs making them prone to such diseases as cholera, dysentery and typhoid, (UNEP, 2000).

Accrding to an Uzbek, "if you run out of water, you run out of life". And for Kofi Annan, former UN Secretary General, "access to a secure, safe and sufficient source of fresh water is a fundamental requirement for the survival, wellbeing and socio-economic development of all humanity. Yet, we continue to act as if fresh water is a particularly abundant resource". The former Nigerian senate president, David Mark in his own opinion stated that a state that fails to provide water for her citizens should be taken to court. Environmentally benign methodologies in treatment are being put in place using Green Chemistry principle to improve the supply and quality.

For over fifty years, food production has kept ahead of rising demand but today in a world where two-thirds of the people depend on rice, wheat and maize as their staple food, many countries are finding it difficult to produce enough food to feed their populations from the existing land and water resources. According to the FAO, world food production will have double in order to provide for 7.8 billion people expected by 2025. About 1.3 billion people living in absolute poverty areas are without good standard of living and one-fifth of the world's population will continue to suffer malnutrition, disease and illiteracy, (FAO, 2001).

The historical practice by farmers and agriculturists to achieve food sufficiency in the world comes with significant environmental consequences. Continued development of compounds to improve agricultural practices and efficiency by green chemistry will be one essential component of achieving sustainable agricultural systems to meet the needs of the additional billions expected to populate the planet.

Energy needs will continue to rise in order to take care of developmental efforts and the growing world population. All energy use has some negative impact on the environment. Burning fossil fuels such as coal and oil produces emissions of green-house gases and acids which results in global warming and acid rains. Fossil fuels are also responsible for urban air pollution (smog) and its associated health hazards. Nuclear power plants expose the environment to low levels of radiation during many stages of the nuclear fuel cycle. This also poses serious risks of major accidents such as Chernobyl in the former USSR, Bhopal in India and recently Fukushima in Japan. Hydroelectric dams can flood vast areas of land and cause damage to aquatic ecosystems, (Anastas and Warner, 1998; WEPS, 2001, 2002) [3]. This negative impact does not only affect the environment, it also create burden on humans as the cost of externalities are borne by parties other than the originators of these plans. Thus, by comparison, renewables such as solar and wind energy have smaller impact on the environment. The use of catalyst is a common way to minimize energy use because with catalysts, reactions can be more efficient and selective. This provides an enormous energy savings while reducing the risks of explosions and other high temperature hazards.

Greenhouse gases occur naturally in the environment and also result from human activities. By far the most abundant greenhouse gas is water vapor, which reaches the atmosphere through evaporation from oceans, lakes, and rivers. The amount of water vapor in the atmosphere is not directly affected by human activities. Carbon dioxide, methane, nitrous oxide, and ozone all occur naturally in the environment, but they are being produced at record levels by human activities. Other greenhouse gases do not occur naturally at all and are produced only through industrial processes. Human activities also produce airborne particles called aerosols, which offset some of the warming influence of increasing greenhouse gases.

Human-made greenhouse gases include chlorofluorocarbons (CFCs), a family of chlorine-containing gases that were widely used in the 20th century as refrigerants, aerosol spray propellants, and cleaning agents. Scientific studies showed that the chlorine released by CFCs into the upper atmosphere destroys the ozone layer. As a result, CFCs are being phased out of production under a 1987 international treaty, the Montréal Protocol on Substances that Deplete the Ozone Layer. CFCs were mostly banned in industrialized nations beginning in 1996 and will be phased out in developing countries after 2010. New chemicals have been developed to replace CFCs, but they are also potent greenhouse gases. The substitutes include hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and perfluorocarbons (PFCs).

In 1988 the United Nations Environment Program (UNEP) and the World Meteorological Organization (WMO) established the Intergovernmental Panel on Climate Change (IPCC). The panel comprises thousands of the top climate scientists from around the world and releases a report every six years describing the state of scientific knowledge on global warming. The IPCC's Fourth Assessment Report, released in 2007, offered the strongest scientific consensus to date on global warming. The panel concluded that it is "very likely" (more than 90 percent probability) that human activities are responsible for most of the warming since the mid-20th century; that it is "extremely unlikely" (less than 5 percent probability) that the warming is due to natural variability; and that it is "very likely" the warming is not due to natural causes alone. This level of certainty is extremely high, given the complexity of the climate system and of the influence of human activities on the climate, (Watson, 2001) [18].

A study published in the *Proceedings of the National Academy of Sciences* warned that climate models used to project future global warming may have been overly optimistic. The study found that atmospheric carbon dioxide levels had increased 35 percent from 1990 to 2006, a rate of increase far higher than most climate models had assumed.

Hazardous wastes mean many things to different nations but basically, hazardous wastes are a type of solid waste. Solid wastes are defined quite broadly and may include solids, sludge, liquids, or gases. Wastes that are not considered solid waste include domestic sewage or wastes that pass through a publicly owned treatment works, industrial discharges, irrigation water, nuclear materials, mine wastes remaining in the ground, recycled sulfuric acid, and some other recycled materials. Others are radioactive and medical wastes, (USEPA, 2002).

Hazardous wastes are generated by nearly every industry; those industries that themselves generate few hazardous wastes nonetheless use products from hazardous waste generating industries. Industry is not alone in generating hazardous wastes. Agriculture produces such wastes as pesticides and herbicides and the materials used in their application. Household sources of hazardous wastes include toxic paints, flammable solvents, caustic cleaners, toxic batteries, pesticides, drugs, and mercury from broken fever thermometers.

Bio-accumulation of these persistent hazardous wastes/chemicals leads to diseases of immunological effect. This is especially so when these chemicals leach into the underground soils. The best way to eliminate hazardous wastes is not to generate them in the first place. For example, improvements have been made in the production of integrated circuits: The toxic chlorinated hydrocarbons commonly used in the 1970s were replaced in the 1980s by less toxic glycol ethers and in the 1990s by low-toxicity esters and alcohols. Furthermore, the gains of green chemistry will be brought to bear on new disposal methodologies, (Devito and Garrett, 1996) [20].

Conclusion

The growth of green chemistry has continued at an amazingly rapid pace in recent years, but it must be put into context. While there are numerous fine examples of how green chemistry is being used for the benefit of industry, the environment, and society, they constitute only a small fraction of the unrealized potential. Advances made in green chemistry in the consideration of energy usages and resource consumption in designing safer and friendlier products will allow for real-time in-process monitoring and control.

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