Exam 1 (Course 096125 (095857))

Introduction of Green and Sustainable Chemistry

Solutions.

1. Answer - Between the different definitions of sustainability I prefer the original one: **Sustainability - "Development that meets the needs of the present without compromising the ability of future generations to meet their own needs." (from *Butland Report for the World Commission on Environment and Development (1992)*)** because it focus on the need to meet our goals and activities in relation to future generations needs, suggesting how the precautionary principle is important when introducing or proposing new solutions to the present needs also in the areas of new technologies. At the same time it propose a development, so is a proactive trend which require careful studies and investigation to ascertain the real sustainable application.

In my opinion another good definition of **Sustainable development is a dynamic process which enables people to realize their potential and improve their quality of life in ways which simultaneously protect and enhance the earth's life support systems" (*from Forum for the Future*)** because it focus on a dynamic process which imply situations of tray and errors but under strictly controlled design in order to reduce the risks, along the entire life cycle, in the use of any chemicals, materials, and in applying activities which can have influence on health and safety.

Examples: 1) Sulfur content reduction in fuels by petrochemical industries; 2) use of liquid CO_2in dry cleaning; 3) Use of natural fiber of hemp for composite panel in building.

2. Answer - Several chemicals have a natural cycle: all compounds directly produced from living cells in their metabolism (i.e. glucose, lactic acid, glycine (the simplest amino acid), etc.) but also any inorganic material involved in geological cycles (i.e. carbon dioxide; mineral ores; silicate rocks, etc.). Selecting glucose as an example, its cycle starts from the photosynthesis reaction, in which carbon dioxide is combined with water under the influence of light, as energy source, in plants (via complex photosynthetic apparatus), to produce glucose and oxygen with the following stoichiometry: $6\ CO_2 + 6\ H_2O \rightarrow \{CH_2O\}_6 + 6\ O_2 \quad \Delta H = +440$ kJ (requires energy provided from light). The cycle of glucose inside cells is very complex and involves the formation of its polymers (cellulose and starch) and a large variety of small chemicals (metabolites), but also the generation of energy for living needs of organisms through the oxidation catabolic process of respiration: $\{CH_2O\}_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O\ \Delta H = -440$ kJ (produces chemical energy stored as adenosine triphosphate, ATP). Human has modified this cycle in quite extensive way introducing new bio-derived products by chemical functionalization of polymers, oligomers and glucose monomer (i.e. nitrocellulose, Viscosa, starch derived biodegradable polymers, surfactants from glucose and oils, lactic acid by fermentation of glucose, etc.).

An example of natural cycle of an inorganic compound is the cycle of sulfur element. This element occurs in nature under three main oxidation states: as element (S_8, N.O. = 0) in large deposits from biological origin or in volcanic vents, as sulfate ion (SO_4^{2-} , N.O. = +6) when any combined forms of the element is exposed for long time to atmospheric oxygen, and as sulfide ion (S^{2-} , N.O. = -2)) under reducing conditions in lower earth crust. The cycling between these three forms depends on the environmental conditions in extended geological cycles, but involves also biological cycles because sulfur is an essential element for living organisms (for example in proteins, cofactors, vitamins, etc.). A relevant example of these bio-processes on sulfur can be found in the vast deposits of sulfur element produced by sulfur bacteria in stagnant waters, which represents now the main source of this element for the industry needs. Man has modified this complex natural cycle introducing the synthesis of sulfuric acid (the chemical produced by man in largest amounts) and developing a large variety of derived products and materials for a wide range of dispersive industrial and consumer applications. Unfortunately, nearly all sulfur mined is dissipated or discarded.

3. Answer - Biomimicry is the belief that the future of material design and use can be found in the design of the natural world around us. The concept underscored by this approach is that after 3.8 billion years of research and development, living organisms have developed key solutions to survive at best in the hearth environment, failures are fossils, and what surrounds us is the secret to survival. In biomimicry, we look at nature as model, measure, and mentor. Biomimics consult organisms; they are inspired by an idea, be it a physical blueprint, a process step in a chemical reaction, or an ecosystem principle. Borrowing an idea is like copying a picture - the original image can remain to inspire others.

The aims of biomimicry is therefore in large part in the same directions of green chemistry goals because the proposed solutions are efficient, just optimized and just verified in natural environment, therefore intrinsically more safe or less harmful. It has been found that chemical transformations involved in biological metabolism were strongly improved in evolution to reach high yield and high atom economy. ATP cycling in cells is an astonishing example of the efficient way that organisms have developed to produce, store, and use energy for the metabolism of any living cell. This molecule is produced and destroyed at level of several kilograms each day in human body with energy efficiency close to 100%.

Examples: (a) Velcro product: mimics the burrs of bardane fruit in which the tiny hooks on the end of the burr's spines caught anything with a loop - such as clothing, hair or animal fur.

(b) The Lotus Effect: chemically treat the surface of plastics and metal were develop to evoke the effect present on the surface of lotus leaves are bumpy, which causes water to bead as well as to pick up surface contaminates in the process.

5. Answer - The life cycle of a plastic bottle start from **Raw Material Extraction** (i.e. when the crude oil and natural gas (NG) are extracted from the environment). Then oil and NG are **transported** to a refinery where they are transformed in commodity chemicals (having the structure of the monomer) to be polymerized. In specialized industry the monomers are converted to polymers in specialized **Manufacturing** plant by a polymerization process, which varies depending on the different type of monomer. Normally (in other factories) the polymer is converted into a container by a specific **Manufacturing** process (i.e. extrusion, injection molding, etc.). For instance, in injection **molding** the plastic granules or pellets are forced into a heating hopper, which liquefies them down pushing the liquefied plastic into a press that molds the bottle. Blow molding is similar to direct injection only that its uses an air jet to blow the liquefied plastic film into the mold. It is usually used to create hollow shapes. The bottles are then transformed in the required **packaging**: they are disinfected, filled, capped, branded, and packed, ready for transportation. The whole process is done by specialized machines, which clasps the bottles from the top and conveys them to the filling machine for fill up with the prescribed amount of water. The bottles, sold through vendors, are then consumed (**Use**). After being drained, the vast majority of these plastic bottles become trash and end up in dumpsters, **landfills** or **wasted** and end up in the ocean wreaking havoc on ocean ecosystems and sea animals. In part, they are submitted to **collection** and **separation** from other plastics and send to **recycle,** normally by mechanical methods. Alternatively, when strongly contaminated (or made from polymers of low quality), they are incinerated to **recover energy**.

Two alternatives that can simplify and reduce the life cycle cost can be:

a) Reduction of the amount of the polymer to make the packaging (reduction in the amount of raw material for functional unit), selecting a better design of the packaging or higher molecular weight of the polymer;
b) Reuse the bottle after careful washing and sanitization (a procedure typically used in glass packaging).

7 Answer - In organic chemistry there are several representative functional groups, i.e. Hydroxyl (-OH, polar and hydrogen bonding group), Carbonyl (-C=O, polar with electrophilic center at carbon atom able to add nucleophiles and oxygen involved in hydrogen bonding and addition to electrophiles), amino ($-NH_2$, basic and nucleophilic group), carboxylic acid (COOH, acid group which lose protons to solvent or other basic molecules). The last two groups are present together in amino acids ($R-CH(NH_2)COOH$) the building blocks of proteins having different R groups. The first group is typical of alcohols and it is present in relevant compounds like glycerol and ethanol. The first and second groups are together present in saccharides, i.e. glucose or arabinose.

Heavy metals react with functional groups like COOH, NH_2, but also with SH (thiols) affording complexes of higher stability when more of these functional groups belong the same molecule (ligand). Typical is the ethylenediaminetetraacetic acid (EDTA, an hexadentate ligand with 2 N and 4 O atom centers). Another example is the 2,3-dithiosuccinic acid (succimer, a dithiol compound used in the decontamination of heavy metals, i.e. Hg or Pb).

9 Answer - Acute toxicity is the toxicity observed at high levels of exposure over a short period of time, whereas the chronic toxicity is the toxicity observed when peoples are exposed at many repeated doses of a chemical, generally to lower levels, over a long period of time.

The potency of acute toxicity is commonly expressed in term of LD_{50} (mean lethal dose that causes the death in 50% of the population of the species exposed under defined conditions of the test). Other data based on dose-response curves can also be used, i.e. LC_{50}, IC_{50}.

The potency of chronic toxicity is commonly expressed in term of EC_{50} (after 15 days or 24 hrs or similar long times). An indirect evaluation of chronic toxicity is the NOAEL corresponding to the highest dose that does not cause a toxic effect (i.e. no observed (adverse) effect). To establish a NOEL requires multiple doses, a large population and additional information to make sure that absence of a response is not merely a statistical phenomenon. LOEL is the lowest observed effective dose on a dose-response curve.

Examples of acute toxic chemicals are hydrogen cyanide, hydrogen sulfide, nitrogen dioxide, ricin, organophosphate pesticides, arsenic, carbon monoxide, etc. For example, arsenic is one of the most toxic metals derived from the natural environment (LD_{50} = 15 mg/kg (rat, oral)). The major cause of human arsenic toxicity is from contamination of drinking water from natural geological sources rather than from mining, smelting, or agricultural sources (pesticides or fertilizers). The maximum permissible limit is a concentration of 50 µg/liter.

Example of chronic toxic chemicals are mercury, lead, formaldehyde, etc.. Lead is a heavy metal used for many years in paints, gasoline (as tetraethyl lead - now banned), and pottery glazes. Chronic studies indicate that this metal has harmful chronic effects on the nervous system of human (the disease is known as saturnism and affect particularly children for their low body weight and likely longer exposure time). Ancient romans, which have used lead to transport water in house, have evidenced symptoms of this disease and attribute the above mentioned term. Cancer is another example of chronic effect.

12 - Solution:

Life Cycle Analysis

Material production:

$E_{material} = E_{steel} + E_{magnesium} + E_{polyurethane} + E_{PVC} + E_{other}$

$E_{current}$ = 10 kg × 40 MJ/kg + 0 kg × 285 MJ/kg + 3 kg × 72 MJ/kg + 2 kg × 65 MJ/kg + 10 kg × 93 MJ/kg

= 400 MJ + 0 MJ + 216 MJ + 130 MJ + 930 MJ

$E_{current}$ = **1676 MJ**

E_{new} = 4 kg × 40 MJ/kg + 3 kg × 285 MJ/kg + 3 kg × 72 MJ/kg + 2 kg × 65 MJ/kg + 8 kg × 93 MJ/kg

= 160 MJ + 855 MJ + 216 MJ + 130 MJ + 744 MJ

E_{new} = **2105 MJ**

Manufacturing Phase Data

E_{mfg} = **500 MJ** for both the current and new designs

Use Phase Data

E_{use} = 1.0 MJ/(kg × 1000 km) * 180,000 km × W_{IP}

$E_{current}$ = 1.0 MJ/(kg × 1000 km) * 180,000 km × 25 kg
= **4500 MJ**

E_{new} = 1.0 MJ/(kg × 1000 km) * 180,000 km × 20 kg
= **3600 MJ**

End of Life Phase Data

E_{eol} = **10 MJ** for both the current and new designs

Total Life Cycle Energy

E_{total} = $E_{material}$ + E_{mfg} + E_{use} + E_{eol}

$E_{current}$ = 1676 MJ + 500 MJ + 4500 MJ + 10 MJ
= **6686 MJ**

E_{new} = 2105 MJ + 500 MJ + 3600 MJ + 10 MJ
= **6210 MJ**

Therefore we can see that the new design does lower the life cycle energy of the instrument panel.