

B.SC SEM – VI CHEMISTRY HONOURS

PAPER : DSE – 3

GREEN CHEMISTRY

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Green chemistry reduces pollution at its source by minimizing or eliminating the hazards of chemical feedstocks, reagents, solvents, and products.

This is unlike cleaning up pollution (also called remediation), which involves treating waste streams (end-of-the-pipe treatment) or cleanup of environmental spills and other releases. Remediation may include separating hazardous chemicals from other materials, then treating them so they are no longer hazardous or concentrating them for safe disposal. Most remediation activities do not involve green chemistry. Remediation removes hazardous materials from the environment; on the other hand, green chemistry keeps the hazardous materials out of the environment in the first place.

If a technology reduces or eliminates the hazardous chemicals used to clean up environmental contaminants, this technology would qualify as a green chemistry technology. One example is replacing a hazardous sorbent [chemical] used to capture mercury from the air for safe disposal with an effective, but nonhazardous sorbent. Using the nonhazardous sorbent means that the hazardous sorbent is never manufactured and so the remediation technology meets the definition of green chemistry.

Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

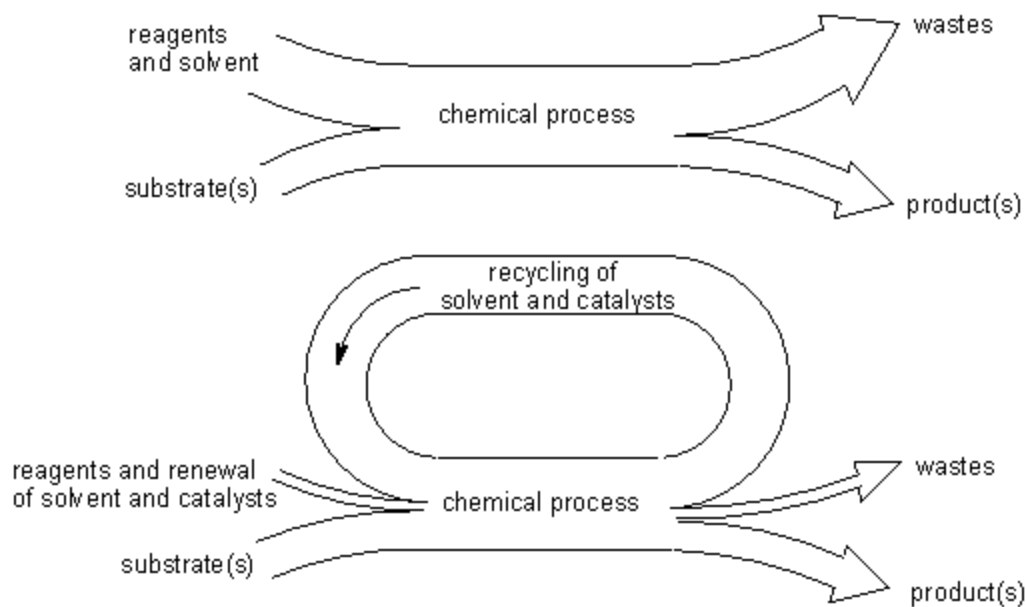
In Green Chemistry the environmental impact of a reaction or the efficiency of a reaction or a chemical process can be quantified by a number of parameters [5]. Of all those that have been defined, here we will highlight the “E factor” and “atom economy.”

12.4.1 E factor

One of the first parameters for evaluating the environmental impact of a chemical transformation is the term “E factor”, which was introduced by R. Sheldon . The concept is quite simple and easy to understand, and it has been applied mainly to the industrial sector. It is a measure of the waste generation in chemicals manufacture. The E factor is calculated by dividing the total mass of waste produced in the preparation of a compound by the total mass of product produced or synthesized. Waste is defined as everything but the desired product. Chemical yield is considered together with reagents, solvent losses, all process aids, and, in principle, even fuel used, although this item is often difficult to quantify. There is one exception: water is generally excluded from the calculation of the “E factor.” For example, when considering an aqueous waste stream, only the inorganic salts and organic compounds contained in the water are counted, while the water itself is excluded. The lower the E value, the lower the waste produced and the lower the environmental impact of the process.

$$(12.1) E \text{ Factor} = \frac{\text{Total mass of wastes(Kg)}}{\text{Mass of products(Kg)}}$$

A typical chemical process generates products and wastes from raw materials such as substrates, solvents and reagents. If most of the reagents and the solvent can be recycled, the mass flow looks quite different:



Thus, the prevention of waste can be achieved if most of the reagents and the solvent are recyclable. For example, catalysts and reagents such as acids and bases that are bound to a solid phase can be filtered off, and can be regenerated (if needed) and reused in a subsequent run. In the production of chemical products on very large scale, heterogeneous catalysts and reagents can be kept stationary while substrates are continuously added and pass through to yield a product that is continuously removed (for example by distillation).

The mass efficiency of such processes can be judged by the E factor (Environmental factor):

$$\text{E factor} = \frac{\text{Mass of wastes}}{\text{Mass of product}}$$

Whereas the ideal E factor of 0 is almost achieved in petroleum refining, the production of bulk and fine chemicals gives E factors of between 1 and 50. Typical E factors for the production of pharmaceuticals lie between 25 and 100. Note that water is not considered in this calculation, because this would lead to very high E factors. However, inorganic and organic wastes that are diluted in the aqueous stream must be included. Sometimes it is easier to calculate the E factor from a different viewpoint, since accounting for the losses and exact waste streams is difficult:

$$\text{E factor} = \frac{\text{Mass of raw materials} - \text{Mass of product}}{\text{Mass of product}}$$

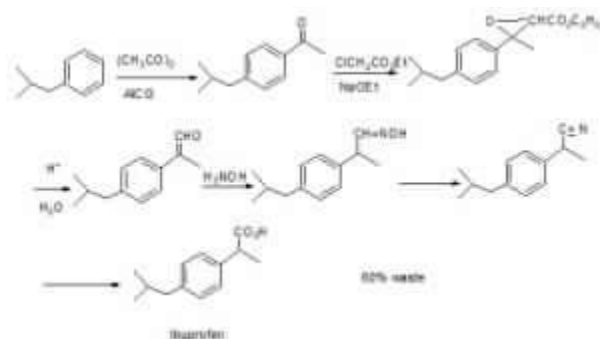
In any event, the E factor and related factors do not account for any type of toxicity of the wastes. Such a correction factor (an “unfriendliness” quotient, Q) would be 1 if the waste has no impact on the environment, less than 1 if the waste can be recycled or used for another product, and greater than 1 if the wastes are toxic and hazardous. Such discussions are at a very preliminary stage, and E factors can be used directly for comparison purposes as this metric has already been widely adopted in the industry.

I) Prevention of Waste: It is better to prevent waste formation than to treat it after it is formed. An example is the manufacture of phenol. It used to be made from benzene using sulfuric acid and sodium hydroxide in a multi-stage process with 78% yield; the reaction can be expressed as:



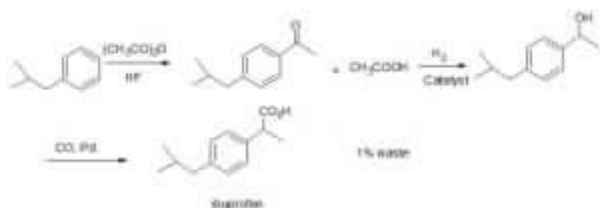
Sodium sulfite is the by-product, can be used in other processes. However, if it is not in demand, that would mean this may not be the most suitable reaction for manufacturing phenol ¹

Another example of green synthesis is the synthesis of ibuprofen. Traditional synthesis of ibuprofen produces 60% waste, as shown below.



SCHEME 1: CONVENTIONAL METHOD OF SYNTHESIZING IBUPROFEN

Alternate green chemistry of ibuprofen produces just 1% waste.



SCHEME 2: GREEN CHEMISTRY METHOD OF SYNTHESIZING IBUPROFEN

Prevent waste: design chemical synthesis to prevent waste, leaving no waste to treat or clean up.

The generation of waste in polymer production arises primarily from three sources: residual monomers due to incomplete reaction conversion, waste from chemicals used during the process but not consumed in the reaction such as solvents and suspending agents, and off-spec material

generated due to excursions from controlled conditions. Residual monomers are especially problematic because of their typically hazardous nature. Since most monomers demonstrate significant toxicity to human health, reducing the residual monomer content is desired to prevent work place exposure as well as exposure to the consumer. Residual monomer removal techniques are generally classified into two categories: chemical methods and physical methods. Chemical methods include the reaction of the residual monomer to generate additional polymer or to produce non-toxic or at least, easily removable compounds. Physical methods include the removal of residual monomer from the polymer by evaporation, by solvent extraction or with the aid of an ion-exchange resin.[2] Extraction of the residual monomer using supercritical carbon dioxide was reported to give better performance than steam stripping techniques. Commonly used chemical methods include ramping the reaction temperature and/or using a finishing catalyst often referred to as a “chaser”. This protocol is usually implemented immediately after the polymerization and may lead to additional costs due to the extra processing stage. Post-polymerization methods and/or chemical monomer removal are often employed to reduce the monomer content before the use of de volatilization processes. Other techniques of this type include post-catalysis procedures followed by spray-drying, and hydrolytic slitting of the monomers followed either by distillation or by the use of an oxidizing agent. In addition to the above-mentioned methods, there are ways to ensure that the monomer consumption in the polymerization is as high as possible.