

Chapter 7. Green Chemistry

by

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Chemical products can be manufactured using a wide variety of synthesis routes. The designer of a chemical process must choose from alternative raw materials, solvents, reaction pathways, and reaction conditions, and these design choices can have a significant impact on the overall environmental performance of a chemical process. Ideal chemical reactions would have attributes such as

- simplicity
- safety
- high yield and selectivity
- energy efficiency
- use of renewable and recyclable reagents and raw materials

In general, chemical reactions cannot achieve all of these goals simultaneously and it is the task of chemists and chemical engineers to identify pathways that optimize the balance of desirable attributes.

Identification of environmentally preferable pathways requires creative advances in chemistry as well as process design. Because the number of choices in selecting reaction pathways is so large and the implications of those choices are so complex, systematic, quantitative design tools for identifying green chemistries are not available. Nevertheless, an extensive body of knowledge concerning green chemistry exists and some qualitative and quantitative design tools are emerging.

Green chemistry, defined as the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances, will be presented in two basic parts - one qualitative and the other quantitative. The first part will describe qualitative principles to be used in developing alternatives - alternative solvents, alternative reactants, alternative chemistries - that may lead to environmental improvements. Section 7.2 provides this overview of qualitative principles that can be used to identify green chemistry alternatives. Section 7.3 describes quantitative, optimization based approaches that have been used to identify environmentally preferable reaction pathways. Finally, Section 7.4 briefly describes the US Environmental Protection Agency's Green Chemistry Expert System, which provides case studies of many of the principles described in this chapter.

Chapter 7 Example Problem

Example 7.1 Calculate atom and mass efficiencies for the Friedel-Crafts reaction shown in Figure 7.5. Assume that the substituent R on the organic chloride is a methyl group.

Solution

To calculate the atom efficiencies, determine the fraction of the carbon, hydrogen, aluminum, chlorine, sodium and oxygen atoms that emerge as product and the fraction that emerges from the reaction as waste.

- Virtually all of carbon (100%) becomes product.
- Most of hydrogen (excluding water in the water wash) becomes product, however if hydrogen used in the water wash is included, virtually all of the hydrogen becomes waste.
- All of the aluminum becomes waste (0% efficiency)
- All of the chlorine becomes waste (0% efficiency)
- All of the sodium becomes waste (0% efficiency)
- One mole of oxygen in the organic chloride is incorporated into the product. Three moles of oxygen in the sodium hydroxide becomes waste. Therefore, excluding oxygen in water, the atom efficiency is 25%.

The mass efficiency can be calculated using atomic weights (ignoring water use).

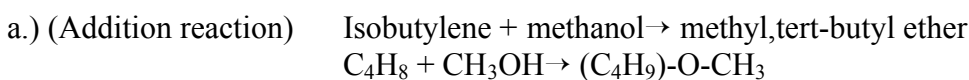
Mass in product = 8 moles carbon * 12 + 10 moles hydrogen * 1 + 1 mole oxygen * 16 = 122

Mass input = 8 moles carbon * 12 + 16 moles H * 1 + 4 moles oxygen * 16 + 1 mole aluminum * 27 + 3 moles chlorine * 35.5 + 3 moles sodium * 23 = 378

Approximate mass efficiency = $122/378 = 0.32$

Chapter 7 Sample Homework Problem

1. The text noted that the atom and mass efficiencies for addition reactions are generally higher than for substitution or elimination reactions. To illustrate this concept, calculate the mass and atom efficiencies for the following reactions:



Calculate mass, carbon, hydrogen and oxygen efficiencies

b.) (Substitution reaction) Phenol + ammonia \rightarrow aniline + water
 $C_6H_5-OH + NH_3 \rightarrow C_6H_5-NH_2 + H_2O$

Calculate mass, carbon, hydrogen, nitrogen and oxygen efficiencies

c.) (Elimination reaction) Ethylbenzene \rightarrow styrene + hydrogen
 $C_6H_5-C_2H_5 \rightarrow C_6H_5-C_2H_3 + H_2$

Calculate mass, carbon, and hydrogen efficiencies

d.) Identify additional industrially significant examples of addition, substitution and elimination reactions; calculate atom and mass efficiencies for these reactions.