

APPENDIX 1: Principles of Life Cycle Assessment

The first part of an LCA is *inventory analysis*. This step entails the identification and quantification of material and energy inputs and outputs for each stage of the product life cycle. LCA models generally limit the scope of inventory analysis to primary inputs and outputs associated with a products life cycle. The environmental implications of secondary and tertiary inventory items, such as facilities and equipment, are therefore neglected in this analysis (14, 18, 54). Although such limitation may be necessary for practicality reasons these inputs may have a significant influence on the potential impacts of product development (54). Experience in incorporating LCD/LCA into product design models indicates that primary inputs will account for the most significant environmental and health impacts (18).

Impact assessment, the second step, is the characterization of the various impacts identified during inventory analysis. In this stage, values are assigned to impacts in order to assess their relative importance (16). This aspect of the LCA can be highly subjective due to limitations regarding data collection and an incomplete knowledge of the comparative influence of specific environmental impacts (55). In addition, subjective consideration of qualitative and quantitative information may produce entirely different results with equally credible analyses (18).

Finally, *improvement assessment* involves identifying options for reducing environmental burden in product systems and developing strategies for environmental improvements in the product life cycle. This stage of the LCA is especially useful in identifying and prioritizing strategies for environmental improvement. However, it is the least developed of the three in the literature (17, 18).

A number of notable LCAs have compared the energy and environmental burden of consumer, commercial, and industrial products. FAL has performed 200 life cycle inventories over the past 19 years (55). The International Standards Organization plans to incorporate an LCA model into its international environmental management standards (ISO 14000), making them especially important for consideration by multinational chemical production/processing corporations (54).

One of the inherent limitations of LCA criteria are their failure to consider the link between the chemical industry and other sectors of our economy. These indirect interactions are inherently important in the life cycle of chemicals and chemical synthetic processes (14, 48, 54). Although indirect interactions will be discussed in terms of chemical feed stocks and energy utilization, the focus of this document is limited to direct interactions. Such extended interactions could be the focus of subsequent work.

APPENDIX 2: Measures of Synthetic Efficiency for Chemical Reactions

The principal measures of synthetic efficiency include reaction yield, reaction selectivity, atom economy, and feedstock conversion (1, 43, 57). Reaction yield is quantified in the following manner:

$$\% \text{ yield} = (\text{actual quantity of products achieved} / \text{theoretical quantity of products achievable}) \times 100$$

The selectivity of a chemical reaction selectivity is expressed mathematically in the following manner (57):

$$\% \text{ selectivity} = (\text{yield of desired product} / \text{amount of substrate converted}) \times 100$$

Reaction selectivity includes chemo-selectivity (competition between different functional groups), diastereo-selectivity (formation of one diastereomer/control of relative stereochemistry), enantio-selectivity (formation of one pair of enantiomers/control of absolute stereochemistry), regio-selectivity (ortho vs. para substitution in aromatic rings/orientational control of two reacting partners), and stereo-selectivity (enantio-selectivity and diastereo-selectivity combined) (43, 57). These selectivity parameters define the length of a sequence of reactions which constitute a synthetic strategy (43).

Atom economy, or atom utilization, a frequently overlooked parameter of synthetic efficiency, is described as the number of atoms of reactants that appear in the products (43). A related concept is percent feedstock conversion, which is defined as percent reactants converted into desired reaction products per reaction cycle. Atom economy is expressed mathematically in the following manner (57):

$$\% \text{ atom economy} = (\text{molecular weight of desired products} / \text{molecular weight of all products}) \times 100$$

Atom economy is defined as the maximum utilization of reactants for the production of desired reaction products. However, reaction yields lower than 100% often limit the potential atom economy to less than 100% (57). Atom economy is an important strategy for P2 in chemistry because it promotes efficient use of feedstocks and elimination or reductions in undesirable reaction co-products and waste. Comparison of atom economy on the basis of theoretical yield is a potential parameter to help evaluate the environmental impact of alternative reactions (57).

APPENDIX 3: Chemical Categories of EPA's SMART Review Process (59)

TIER I – EXTREMELY TOXIC, REGULATED SUBSTANCES

Note: Toxicity in the range of parts per billion or less)

- Arsenic Compounds
- Beryllium Compounds
- Cadmium Compounds
- Dioxins, Benzofurans (includes all brominated and chlorinated isomers containing 4-8 halogens)
- Hydrogen Fluoride
- Hydrogen Sulfide
- Organomercurials
- Phosgene
- Sarin (Isopropyl methylphosphonyl Fluoride) and Other Highly Neurotoxic Organophosphorus compounds
- Other Potentially Extremely Toxic Regulated Substances

TIER II – CHEMICALS OF MODERATE TO HIGH CONCERN

- EPCRA Section 302 List of Extremely Hazardous Substances (See 40 CFR Part 355, Appendix A & B)
- EPCRA Section 313 List of Toxic Chemicals (See 40 CFR Part 372)

- OPPT List of Categories of Concern

- | | |
|--|--|
| – Acid Chlorides | – Acid Dyes |
| – Acrylamides | – Acrylates/Methacrylates |
| – Aliphatic Amines | – Alkoxysilanes |
| – Aminobenzothiazole Azo Dyes | – Amphoteric Dyes |
| – Anhydrides, Carboxylic Acid | – Anilines |
| – Anionic Surfactants | – Benzotriazoles |
| – Benzotriazole–Hindered Phenols | – Borates |
| – Cationic Dyes | – Cationic (Quaternary Ammonium) Surfactants |
| – Dianilines | – Diazoniums |
| – Dithiocarbamates | – Epoxides |
| – Esters | – Ethylene Glycol Ether |
| – Hydrazines and Related Compounds | – Hindered Amines |
| – Imides | – Isocyanates |
| – β -Naphthylamines (Monosulfonated) | – Neutral Organics |
| – Nickel Compounds | – Nonionic Surfactants |
| – Peroxides | – Phenols |
| – Polyanionic Monomers and Polymers | – Polycationic Polymers |
| – Polynitroaromatics | – Rosin |
| – Substituted Triazines | – Stilbene [Derivatives of 4, 4-bis (triazin-2-ylamino) –] |
| – Vinyl Esters | – Vinyl Sulfones |
| – Soluble Complexes of Zinc | – Zirconium Compounds |

TIER III – CHEMICALS OF LOW TO MODERATE CONCERN

Note: Non-regulated, Potentially Hazardous Substances

- Chemicals which are neither regulated nor innocuous
- Non-regulated substances where there is a question of whether they are relatively innocuous or not

TIER IV – CHEMICALS OF LOWEST CONCERN

Note: Relatively Innocuous Chemicals

- Na, K, Mg, Ca Salts of Chlorides, Sulfates, and Carbonates
- Water, Nitrogen, Carbon Dioxide
- Certain high molecular weight condensed phase polymers such as polyethylene and mylar (polyethylene terephthalate)

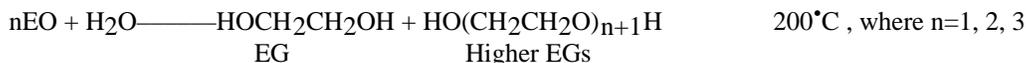
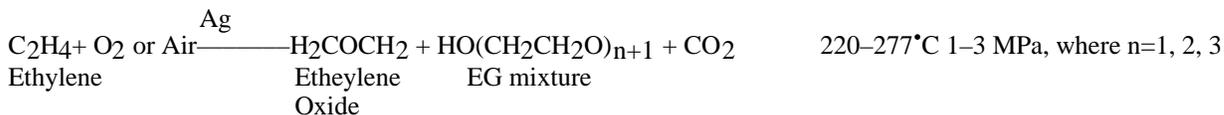
APPENDIX 4: Using Antifreeze Solutions in Internal Combustion Engines

Antifreeze solutions are often called “engine coolants.” This is somewhat misleading terminology as the water content of engine coolants actually provides the total solution its heat absorption and transfer properties. Early in the development of the internal combustion engine water was chosen as a coolant due to its low cost, availability, and favorable heat transfer properties. However, water’s corrosive nature, high freezing point, and 9% to 10% volume expansion upon freezing necessitated the development of additives to prevent damage to engine blocks, water pumps, and radiators (67, 68, 69).

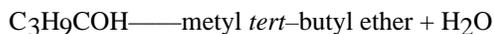
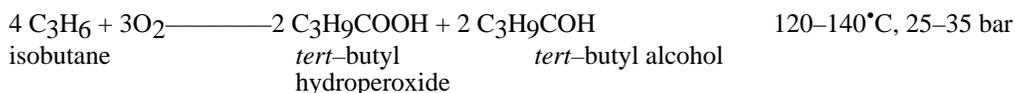
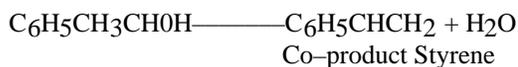
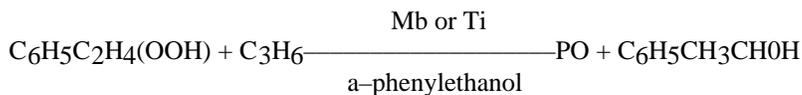
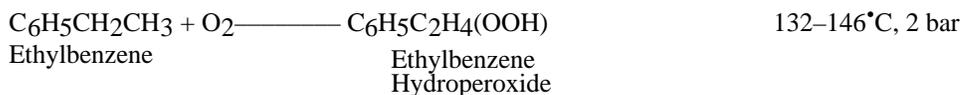
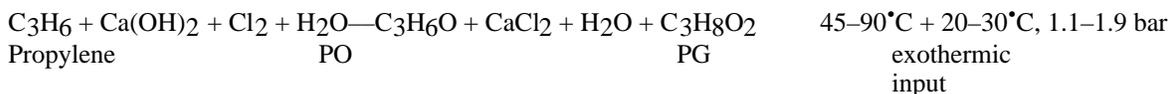
The name “antifreeze” is given to dilute aqueous solutions of PG and EG because of their unusual phase behavior at extremely cold temperatures. When exposed to temperatures below freezing the water in antifreeze solutions will crystallize prior to the glycol–component. This increases the concentration of EG or PG in the liquid phase, resulting in a lower overall freezing point. The dilute EG/PG mixture therefore behaves as a slush over a much wider temperature range than either pure water or glycol product. The boiling point of dilute antifreeze solutions is also higher than water alone, but depends on the mixture of corrosion inhibitors present in the solution (66).

APPENDIX 5: Definition of EG, PG, EO, and PO Reactions (66, 67, 68, 69, 71)

ETHYLENE GLYCOL



PROPYLENE GLYCOL

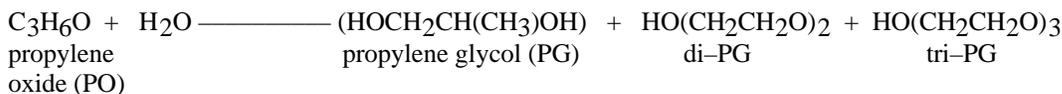


*15 molar excess of water produces mono, di-, and tri- PG in ratio of 100:10:1

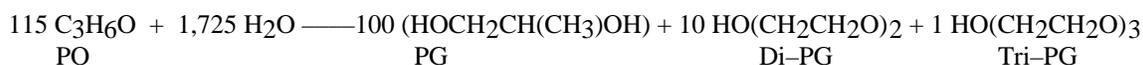
APPENDIX 6: Stoichiometric Calculations for EG and PG Feedstocks (66, 67, 68, 69, 71)

PROPYLENE GLYCOL

- (1) Assumptions:
- 3694 g of PG is goal based on FAL data
 - isobutane hydroperoxidation is the production process
 - 15 molar excess of water produces mono, di, and tri PGs in a ratio of 100:10:1



$$\begin{aligned} 346 \text{ total carbons} &= 100 \text{ (3 carbons in PG)} + 10 \text{ (4 carbons in di-PG)} + 1 \text{ (6 carbons in tri-PG)} \\ 346/3 &= 115 \end{aligned}$$



$$3,694 \text{ g PG} \times 1 \text{ mol}/76 \text{ g} \times 115 \text{ mol PO}/100 \text{ mol PG} \times 58 \text{ g PO/mol} = \mathbf{3241 \text{ g PO} \text{ --or-- } 55.89 \text{ mols PO}}$$

- (2) Assumptions:
- Reactants dissolved in toluene
 - Molybdenum catalyst
 - Selectivity for PO is 80%
 - Propylene conversion is 98% with ten-fold excess of propylene



$$\begin{aligned} 55.8 \text{ mols PO} \times 1/0.80 \times 1/0.98 &= 71.17 \text{ mols TBH} \times 90 \text{ g/mol} = \mathbf{6,405 \text{ g TBH}} \\ 71.17 \text{ mols propylene} \times 42 \text{ g/mol} &= \mathbf{29,891 \text{ g propylene}} \end{aligned}$$

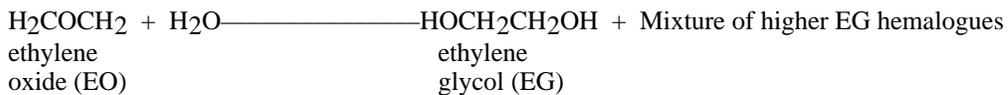
- (3) Assumptions:
- Isobutane generated from mixed butane fraction
 - 48% conversion of isobutane
 - 50% selectivity for TBH, 48% selectivity for TBA, 4% residual selectivity



$$\begin{aligned} 71.17 \text{ mols TBH} \times 1/0.48 \times 1/0.5 \times 4 \text{ mols isobutane}/2 \text{ mols TBH} &= \mathbf{593 \text{ mols Isobutane}} \\ 593 \text{ mols Isobutane} \times 90 \text{ g/mol} &= \mathbf{34,394 \text{ g Isobutane}; 65.5 \text{ mols TBA or } 4845 \text{ g TBA}} \end{aligned}$$

ETHYLENE GLYCOL

- (1) Assumptions:
- 3,877 g (62.53 mols) of EG is goal based on FAL data
 - EG selectivity is 90%, 100% conversion of feedstocks



62.53 mols PO x 44 g/mol = 2751 g PO

- (2) Assumption:
- Oxidation with pure oxygen
 - 7% to 15% conversion of ethylene
 - 80% selectivity for PO



62.53 mols ethylene x 1/0.80 x 1/0.07 x 28 g ethylene/mol = **31,265 g ethylene @ 7% conversion**

62.53 mols ethylene x 1/0.80 x 1/0.15 x 28 g ethylene/mol = **14,590 g ethylene @ 15% conversion**

