V. CASE STUDY: COMPARISON OF ETHYLENE GLYCOL VERSUS PROPYLENE GLYCOL-BASED ANTIFREEZE SOLUTIONS

A. Introduction

This case study demonstrates the quanitative and qualitative information collected through application of the multi-disciplinary life cycle framework suggested in the previous section of this document. It analyzes the production and utilization trade-offs associated with ethylene glycol (EG; 1, 2-ethanediol) and propylene glycol (PG; 1, 2-propanediol) based antifreeze products. Specifically, the case study focuses on their use in water-based coolant systems of internal combustion engines[1]. Additional components added to antifreeze products include corrosion inhibitors, anti-foaming agents, coloring agents, and metal and glycol antioxidants (66). The following chemical constituents of EG and PG-based antifreeze formulations are considered in the Franklin Associates, Ltd. (FAL) study[2]:

PG-BASED ANTIFREEZE	% OF TOTAL	EG-BASED ANTIFREEZE	% OF TOTAL
Water	3.20	Water	2.20
Propylene Glycol	94.00	Ethylene Glycol	96.20
Sodium Hydroxide	0.20	Sodium Hydroxide	0.22
Sodium Nitrate	0.30	Sodium Nitrate	0.15
Sodium Silicate	0.29	Sodium Silicate	0.23
Sodium Tetraborate	2.01	Sodium Tetraborate	0.70
		Sodium Orthophosphate	0.30

The term "antifreeze product" refers to the above undiluted chemical formulations. Antifreeze products are diluted with water, typically in a 50/50 ratio, prior to being added to the cooling systems of internal combustion engines. The term "antifreeze solution" refers to aqueous mixtures containing 50% water and 50% antifreeze product[3]. These definitions apply throughout this case study unless indicated otherwise in the text (55, 56).

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[1]Related applications of EG and PG-based products includes their use in refrigeration systems, heat transfer and water heating systems, building air conditioners, solar energy units, automatic sprinklers, snow melting equipment, deicing fluids for planes, water-based paints, pharmaceutical products, and freeze drying apparatus (66, 67, 68, 69).

[2]Percentages are based on approximate weights of chemical constituents in antifreeze solution presented in Table 11 of this case study (55).

[3]To normalize the solutions for freeze protection, FAL uses a dilution ratio of 53% PG product / 47% water in its comparison. Results in the case study indicate which dilution ratio applies.

Applicable data regarding the life cycle of PG and EG antifreeze solutions are limited due to its proprietary nature. Therefore, some aspects of the analysis refer to specific reaction steps, while others apply to the entire life cycle of these solutions. All information obtained from FAL considers the full life cycle of these chemicals. This includes raw material extraction, production of PG and EG, manufacture and disposal of primary and tertiary packaging, filling, disposition, and disposal of spent antifreeze product (55). Data generated in the FAL study applies to the following U.S. production processes for these chemicals[4]:

PG PRODUCTION   Hydrolysis of Propylene Oxide (PO) in Water
EG PRODUCTION   Hydrolysis of Ethylene Oxide (EO) in Water
PO PRODUCTION   Weighted Average of Chlorohydrination, Isobutane
                              Hydroperoxidation, and Ethylbenzene Hydroperoxidation
EO PRODUCTION   Catalytic Oxidation of Ethylene

Other aspects of this case study designate applicable reaction steps. Systems not examined in the FAL study include fuel, energy, and waste associated with production and use of capital equipment, space conditioning, support personnel, and miscellaneous materials and additives that are less than 1% of the net process output (55).

B. Data Collection Methods

Data collection activities are based on the inventory analysis stage of a LCA, but are not limited to environmental and health-related impact categories. Additional data categories include quantification of reaction inputs and outputs, energy requirements, residuals associated with production and utilization, properties of reaction inputs and outputs, reaction economics, and regulatory requirements. Data sources include general literature on antifreeze solutions and constituent chemicals, reference texts, interviews with chemical industry personnel, and two chemical industry subscription databases published by Stanford Research Institute (SRI). These databases, which include the Chemical Economics Handbook (CEH) and the Process Economics Program (PEP), are

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[4]All data regarding EG-based antifreeze presented in the FAL study is calculated based on a U.S. industry average. Similar data for PG-based antifreeze are calculated using a weighted average for production capacity of the following PO processes: isobutane hydroperoxidation (31.4%), ethylbenzene hydroperoxidation (28.5%), and chlorohydrination (40.1%).

available for use by private corporations and some educational institutions. In addition, a LCA and partial impact analysis, published by Franklin Associates, Ltd. (FAL) in August 1994, is the primary resource for data related to energy consumption, environmental emissions, and reaction residuals.

C. Theoretical Needs Analysis

Alternatives to EG and PG should be first considered as the basic component of antifreeze solutions. Prior constituent chemicals of antifreeze solutions included denatured ethanol, synthetic methanol, isopropyl alcohol, glycerol, calcium chloride and other salt solutions, honey and sugar solutions, and hydrocarbon oils such as kerosene. Typically, product availability, rather than cost and performance, was the criterion for using these various chemicals. Following World War II, ethylene glycol and methanol were primarily utilized in vehicles in the U.S. and Western Europe. By 1970 EG-based antifreeze solutions were used almost exclusively by automobile manufacturing all over the world. The main factor for displacing methanol-based products was higher engine operating temperatures, which yielded superior space heating capacity and slight improvements in fuel efficiency. Recently, propylene glycol-based antifreeze products have became popular for use in automotive cooling systems, solar energy collectors, cooling systems of engines operating potable water systems, and refrigeration systems for food and dairy products (66). See Appendix 4 for additional information related to the use of EG and PG-based antifreeze solutions as a coolant of internal combustion engines.

Feedstocks and other aspects of the reaction system that extend the useful life and/or enhance product performance should also considered. In terms of antifreeze products, the type and amount of formulation chemicals, other than the glycol component, will determine the effective product life. Useful life extension of antifreeze products may reduce the number of times consumers replace these solutions, thereby decreasing the number of potential adverse exposures. The feedstocks for both glycol chemicals are derived from non-renewable petroleum and natural gas resources. There are no alternative synthetic pathways for PG or EG that utilize biological or other renewable feedstocks identified at this time.

Finally, evaluation of the overall need for antifreeze solutions should also occur prior to analysis. Internal combustion engines fabricated with materials having greater heat absorbent properties, such as ceramics or composites, could

lessen or eliminate the need for engine coolant systems. If these options are available the analyses should focus on comparing alternative engines fabrication materials with traditional ones. Relevant information regarding advancements in fabrication materials for internal combustion engine was not a part of this case study. However, it could be the focus of research efforts if they become a viable option in the future.

D. Production Summary

Figure 4 summarizes the production processes for both ethylene glycol (EG) and propylene glycol (PG) based antifreeze solutions. The specific EG and PG reaction steps utilized in this case study are described in Appendix 5. Both EG and PG are produced from the refining of crude oil and natural gas. They are processed at an ethylene cracker into propylene and ethylene feedstocks. In addition, off gases from the refining process may contain recoverable propylene, which can be diverted to PO production facilities. (69). In 1993, 73% of ethylene and 28% of propylene were produced from natural gas liquids and refinery off-gases, and the balance was produced from crude petroleum feedstocks (70).

**Figure 4: Summary of Production Processes of
EG- and PG-Based Antifreeze Solutions**
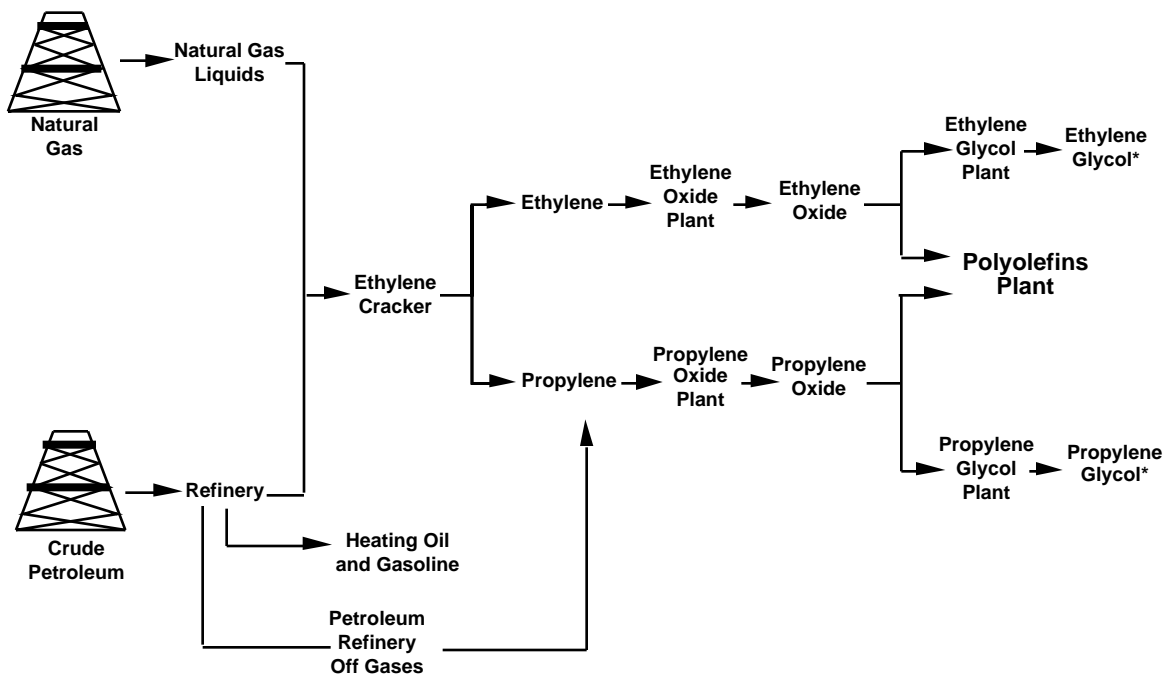
NOTE: * Undiluted EG and PG feedstocks are sent to a formulation facility where they are combined with corrosion inhibitors, anti-foaming agents, and other additives. This final formulation is packaged and shipped to retail outlets or shipped in bulk for packaging by suppliers.

Ethylene and propylene are then processed into ethylene oxide (EO) and propylene oxide (PO), respectively. Present production facilities in the U.S. convert ethylene via catalytic (silver) oxidation to EO. The traditional chlorohydrin process is being replaced by this direct oxidation process due to unfavorable reaction costs and production of chlorine waste water. Alternate routes of production are presently under development, but these processes are not appropriate for industrial applications[5] (71). PO production facilities utilize the chlorohydrin process, co-product processes (isobutane hydroperoxidation, ethylbenzene hydroperoxidation), hydrogen peroxide routes, and direct oxidation (72).

Following production of EO and PO, both chemical intermediates are converted into their glycol equivalent through similar hydration processes. Both reactions produce higher glycols (di, tri, tetra) because the mono-PG/EG products cannot be removed from the reactor quickly enough. However, these additional glycol products are separated from the desired mono-glycol counterpart through a series of distillation and purification processes (68). Following these steps, PG and EG are shipped to regional formulation and packaging facilities. The formulation process occurs in a batch operation utilizing tanks equipped with agitator and heating coils to facilitate dissolution of additives. The final EG/PG-based antifreeze product is then packaged and shipped to retail and commercial locations (66).

At the present time there are no viable alternative feedstocks, other than crude oil and natural gas, which can be utilized in the production of EG or PG-based antifreeze. Current research focuses on optimizing reaction conditions and reducing the energy consumption of reactions through the use of alternative catalysts. The abundant supply of present feedstock sources, existing infrastructure, and reasonable price have not justified additional research on non-petroleum sources (67, 69).

E. Quantification of Reaction Inputs and Output

Table 11 compares component weights for reaction inputs, antifreeze products, and packaging material associated with 1000 gallons of EG and PG-based antifreeze solution. Calculations for feedstocks and other reaction inputs for Table 11 are based on FAL data and stoichiometric calculations represented in Appendix 5.

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[5]Past production processes for EO include a chlorohydrin route, synthesis via a formaldehyde and carbon monoxide pathway, and a direct oxidation reaction. These production methods are not currently utilized by modern facilities due to the enhanced reaction efficiency and lower production cost of the present alternatives (67).

Limitations associated with the data from Table 11 and Appendix 5 make it difficult to compare these two chemical reaction systems. It was not possible to compare the reaction equations and relevant parameters stated in Appendix 5 with those utilized by FAL. In addition, FAL's weighted average technique for the PO production processes does not lend itself to further feedstock calculations. In estimating feedstock calculations based on stoichiometric calculations, a singular PO reaction route (isobutane hydroperoxidation) has to be chosen. Therefore, the calculations based on the reaction steps in Appendix 5 are not necessarily consistent with FAL, nor do they reflect present production capabilities. Feedstock and reaction input data are also incomplete with regard to reaction co-products, catalysts, and solvents. Given the inconsistencies associated with feedstock and reaction input data, it is not appropriate to draw direct comparisons between aspects of these aspects two reaction systems. A more equivalent evaluation of glycols and other feedstock is to compare the quantity of crude oil or natural gas necessary to produce 1000 gallons of each antifreeze solution. These limitations are discussed further in Section K of this case study.

The FAL data represents average formulations utilized in North America. The amount and type of glycol and inhibitor compounds vary according to brand. In terms of the corrosion inhibitor compounds, the PG solution contains greater amounts in three of the four common categories with significant differences between sodium tetraborate (PG: 92.8 lbs/1,000 gal.; EG: 31.1 lbs/1,000 gal.) and sodium nitrate (PG: 13.8 lbs/1,000 gal.; EG: 6.7 lbs/1,000 gal.). This evaluation is not altered when the PG data is recalculated using a 50% water / 50% PG product dilution ratio (sodium tetraborate: 87.5 lbs, sodium silicate: 12.6 lbs, sodium nitrate: 13.0 lbs, sodium hydroxide: 9.1, and water: 139 lbs). This recalculation lowers the total amount of PG in the product from 4,316 to 4,072 lbs, which is significantly less than the EG component (4,274 lbs) of the similarly diluted solution. Although the primary and tertiary packaging are greater in all categories for the PG solution, recalculation using equivalent dilution ratios results in data values identical to those of the EG solution (55).

TABLE 11:   Component Weights for EG- and PG-based Antifreeze Product and Packaging System (55)

	EG (lbs/10^3gallons)	PG (lbs/10^3gallons)
Feedstocks and other Reaction Inputs		
Ethylene	14,590.00 to 31,265.00	–
Ethylene Oxide	2,751.00	–
Silver Catalyst	n/a	–
Molydenum Catalyst	–	n/a
Isobutane	–	34,394.00
tert–butyl hydroperoxide	–	6,405.00
Propylene Oxide	–	3,241.00
Propylene	–	29,891.00
Methyl Tert–butyl Ether (co–product)	–	n/a
Antifreeze Product		
Ethylene Glycol	4,274.00	–
Propylene Glycol	–	4,316.00
Sodium Tetraborate	31.10	92.80
Sodium Silicate	10.20	13.30
Sodium Nitrate	6.70	13.80
Sodium Orthophosphate	13.30	–
Sodium Hydroxide	9.80	9.60
Water	95.90	147.00
Water Added by Consumer	4,442.00	4,072.00
Primary Packaging		
HDPE Containers	162.00	171.80
Polypropylene Cap	5.10	5.37
Bleached Paperboard Cap Liner	0.77	0.80
Aluminum Foil & HDPE Film Safety Seal	0.11	0.12
Tertiary Packaging		
Corrugated Cardboard	166.60	176.20
LDPE Stretchwrap	2.00	2.10

Notes: • Antifreeze formulation represents an average for North America (50 EG product ∕ 50 water; 53% PG product ∕ 47% water)

• Feedstock data calculations based on equations mentioned in Appendix 5 depend on percent conversion and selectivity of process

• One corrugated container equals six one–gallon HDPE containers

• Stretchwrap for one pallet wraps 36 corrugated containers or 216 HDPE containers

• HDPE – high density polyethylene; LDPE – low density polyethylene

• FAL assumes that secondary packaging as materials, such as display cases and signs utilized at retail outlet, is not a part of antifreeze product life cycle.

• Data for PG feedstock calculations based on isobutane hydroperoxidation reaction for PO

• n∕a represents unavailable data

F. Energy Requirements

The energy requirements for the production of 1,000 gallons of diluted EG and PG antifreeze solutions are described in Table 12. Process energy is consumed during the manufacturing of the chemical product. Transportation energy is consumed during transport of all chemicals and materials to and from the processing sites, including energy consumed during transportation of final product to retail establishments[6]. Energy of material resources is the fuel energy equivalent of fossil fuel-derived raw materials (petroleum feedstocks for ethylene/propylene). Fuel energy data are adjusted to account for the extraction, processing, and transport of primary fuels (55).

TABLE 12: Energy (Btu) Requirements for Production and Utilization of 1,000 gallons of EG- and PG-Based Antifreeze Solutions (55)

	Process	Transportation	Material Resource	WTE Credit	Total
EG	63.2	3.9	65.9	(4.6)	128.5
PG	119.6	5.7	69.0	(4.6)	189.7

Notes:
- All numbers expressed in 10^6 Btu
- Dilution ratios are 50% water / 50% EG product, 47% water / 53% PG product
- WTE indicates waste to energy incinerator equipped with energy recovery technology
- 18% of all post recycled municipal solid waste (MSW) is combusted at WTE facilities

Table 13 shows the energy consumption of specific constituents in the EG and PG chemical life cycles. Energy associated with glycol production includes production of feedstocks through fabrication of final undiluted chemical product (55). Chemical formulation energy is consumed as a result of the processing of the EG and PG antifreeze products. Primary packaging energy is consumed from raw material extraction for making the HDPE container, polypropylene cap, bleached paperboard cap liner, aluminum foil, and HDPE safety seal. Tertiary packaging energy is consumed from raw material extraction to the manufacture of corrugated cardboard containers and low density polyethylene (LDPE) stretch wrap. Finally, disposition energy is consumed as a result of post-consumer processing, recycling and reuse, and disposal of spent antifreeze products (55).

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[6]Transportation energy include the energy consumed by consumer to drive to and from the service center where the antifreeze solution is replaced. It excludes energy for the "do-it-yourselfer" to drive to and from retail outlets for purchase of replacement solutions (56).

TABLE 13: Energy (Btu) Requirements for Components of EG- and PG-Based Antifreeze Product and Packaging Systems (55)

	EG Energy	% Total	PG Energy	% Total
Glycol Production	114.6 Btu	86.1	175.2 Btu	90.2
Formulation Chemicals	0.5	0.3	0.8	0.4
Antifreeze Formulation	5.4	4.0	5.0	2.6
Primary Packaging	6.5	4.9	6.9	3.6
Tertiary Packaging	2.6	2.0	2.8	1.4
Disposition	3.5	2.7	3.6	1.8
Total	133.1 Btu		194.2 Btu	

Note: • All numbers expressed in terms of 10^6 Btu
• Dilution ratios are 50% water / 50% EG product, 47% water / 53% PG product

The production of the PG-based antifreeze product results in a 47% greater consumption of energy than EG-based solution. Table 13 indicates that this difference results specifically from the glycol production processes of PG (175.2 Btu) and EG (114.6 Btu). When the dilution ratio of the PG solution is lowered to 50/50 the resulting energy consumption for production is lowered by 10×10^6 Btu. This still represents 40% greater energy consumption for the PG production process (165.2 Btu). Both EG and PG production are involve similar hydration processes. Therefore, the difference in energy consumption seems attributable to the EO and PO reactions (55). However, this observation cannot be validated because energy consumption of the individual EO/PO production processes is not presented in the FAL data. It is further complicated by the fact that the PO energy consumption data represents an average of three different reactions, rather than one actual process. This prevents identification of the true source of the excessive energy consumption in the PG product system.

Table 14 contains the energy sources utilized in the life cycle of 1000 gallons of PG and EG antifreeze product. Natural gas, petroleum, and coal are the major fuel sources for electricity in the U.S. The natural gas energy includes energy of material resources attributed to the extraction and processing of raw materials. These data are only useful if energy consumers were capable of differentiating which energy source they drew upon for their operation. This option does not apply, however, because site-specific energy production data are not accounted for in the FAL study (55).

TABLE 14: **Energy Sources Associated with Production and Utilization of 1,000 Gallons of EG- and PG-Based Antifreeze Solutions (56)**

	Natural Gas	Oil	Coal	Hydro	Nuclear	Wood	Other	*Total*
EG	86.6	29.8	10.8	0.61	4.3	0.96	0.074	133.1 Btu
PG	113.8	44.7	24.5	1.25	8.8	1.02	0.15	194.2 Btu

Note: • All numbers expressed in terms of 10^6 Btu

• Dilution ratios are 50% water / 50% EG product, 47% water / 53% PG product

• Data account for portion of electricity generated at manufacturing facilities & sold to grid

G. Residuals Associated with Production and Utilization

(1) Solid Waste

Table 18 describes the solid waste associated with the production and utilization of 1,000 gallons of EG and PG antifreeze solutions. This includes solid waste generated during all aspects of the product life cycle, such as ash generated at incineration facilities and residual material collected by pollution control devices (55). Process industrial solid waste includes the following sources: wastewater treatment sludges, solids from air pollution control devices, unrecycled trim or waste materials from manufacturing operations, fuel combustion residues from power generation facilities, and resource extraction wastes (55). Fuel-related industrial solid waste includes materials generated from the acquisition and consumption of resources to produce energy. Post-consumer solid waste includes primary and tertiary packaging as well as spent anti-freeze solutions. Recycled materials are accounted for in the overall analysis but excluded from this data (55).

TABLE 15: **Solid Waste Associated with Production and Utilization of 1,000 Gallons of EG- and PG-Based Antifreeze Solutions (56)**

	Industrial Solid Waste Process		Fuel		Post-Consumer Solid Waste		Total Solid Waste	
	(lbs)	(ft^3)	(lbs)	(ft^3)	(lbs)	(ft^3)	(lbs)	(ft^3)
EG	95	1.9	388	7.8	232	13.9	715	23.6
PG	346	6.9	831	16.6	246	14.7	1424	38.3

NOTE: • Dilution ratios are 50% water / 50% EG product, 47% water / 53% PG product

• 55% of corrugated containers are recycled; 19% of unrecycled packaging materials are combusted and 81% landfilled

• 94% of combustion of unrecyclable solid waste occurs at WTE facilities

• Data accounts for hazardous waste production but does not identify quantities

The large difference in solid waste (EG = 715 lbs. vs. PG = 1,424 lbs.) for both the process and fuel categories can be attributed to the greater energy requirements of the PG-based product (56). Packaging requirements for both solutions are similar, resulting in very little difference in post-consumer solid wastes (EG = 232 lbs. vs. PG = 246 lbs.). When equivalent dilution ratios are utilized for both PG and EG (50% glycol/50% water), the amount of post-consumer solid waste becomes equivalent (13.9 lbs./1,000 gallons). However, the process and fuel solid waste for PG remain significantly higher than EG (6.6 and 15.8 lbs./ 1,000 gallons, respectively) (55). Again, these differences may be a factor of the aggregation of the PO production processes.

The data in Table 15 does not differentiate between the amount of hazardous and non-hazardous solid wastes produced in any of these categories (55). This would have provided additional criteria to differentiate EG and PG in terms of reaction efficiency, waste management and disposal costs, and regulatory compliance issues for generators.

(2) Atmospheric and Waterborne Industrial Emissions

Table 16 contains a list of the industrial atmospheric emissions associated with the production of PG and EG antifreeze products. Only those substances identified as regulated pollutants by applicable agencies are accounted for in this table. Amounts of atmospheric pollutants represent actual discharges after exiting pollution control devices (55).

Production of PG antifreeze solutions produces significantly greater atmospheric emissions (i.e., >10%) in 12 of 16 common pollutant categories[7]. Of the pollutants common to both reaction systems, methane is the only one produced at significantly greater levels in the EG process (55). For both PG and EG a greater portion of atmospheric emissions results from process-related wastes, as opposed to fuel-related wastes. The difference in atmospheric pollution production is attributed to the PG processes' higher energy requirements (55). Separate analysis of the individual PO production processes may have altered this assessment.

Table 17 contains the industrial waterborne emissions associated with the production of 1,000 gallons PG and EG antifreeze solution. Waterborne pollutants are reported in terms of average quantities present in receiving water discharges after in-house waste water treatment or treatment at publicly owned treatment

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[7]EG, EO, and ethylbenzene are only associated with EG production. Propylene, PO, and propylene chlorohydrin are only associated with PG production.

works (POTWs). These results include only those materials designated as pollutants by applicable regulatory agencies. There is no distinction as to the minimum treatment level for either in-house or public facilities (55).

PG production results in greater amounts of waterborne wastes than EG in all common categories except for suspended solids. However, there is no significant difference (>10%) in pollutant quantities for the following categories: ammonia, biological oxygen demand, chromium, cyanide, fluorides, herbicides, nitrogen, oil, phosphates, sulfides, and zinc (55). The differences in waterborne wastes are a factor of the feedstocks for the production process for PO and EO, as opposed to the difference in energy consumption (55).

Consideration of equivalent dilution ratios does not significantly alter evaluation of the of the pollutant quantities found in Table 16, but do affect the results found in Table 17 (55). The number of waterborne waste categories where PG has higher levels is reduced from 19 to 9 of the common categories. In addition, quantities of cyanide and fluorides associated with PG become lower than that of the EG process.

The aggregation of the three PO production processes results in accountability for all atmospheric and waterborne pollutants from all three processes. Analysis of one PO production process may have eliminated and/or decreased air and waterborne emissions in these categories. These data also would have been more informative if pollutant categories that applied to the specific PO production processes was identified by FAL. Unfortunately this information is not available for consideration.

Tables 16 and 17 contain several non-descript emissions categories. For example, industrial atmospheric emissions include acids, aldehydes, hydrocarbons, and other organics. Industrial waterborne emissions include acids, herbicides, hydrocarbons, metal ions, oil, pesticides, and suspended solids. Identifying speciation of metals, such as lead and mercury, is also important due to the varying behavior of alternate forms. Such ambiguous characterization of chemicals prevents analysis of their fate and transport in the environment, as well as characterization of toxicity potential to flora and fauna.

TABLE 16: Industrial Atmospheric Emissions Associated with Production of 1,000 Gallons of EG- and PG-Based Antifreeze Solutions[8] (55)

	Process EG (lbs.)	Process PG (lbs.)	Fuel EG (lbs.)	Fuel PG (lbs.)	Total EG (lbs.)	Total PG (lbs.)
acid	–	0.2	–	–	–	0.2
aldehydes *	0.033	0.034	0.26	0.035	0.29	0.39
ammonia	0.015	0.23	0.035	0.068	0.05	0.3
carbon dioxide *	2186	739	9313	17,609	11,499	18,348
carbon monoxide *	1.04	1.09	17.4	26.9	18.5	28
chlorine * ^	8.7E-05	0.0052	–	–	8.7E–05	0.0052
ethylbenzene	–	4.2	–	–	–	4.2
ethylene glycol #	7.29	–	–	–	7.29	–
ethylene oxide #	1.31	–	–	–	1.31	–
hydrocarbons	73.8	92.5	38	66.2	112	159
hydrogen fluoride	1.5E-04	1.6E-04	–	–	1.5E-04	1.6E-04
isobutane	–	6.75	–	–	–	6.75
kerosene *	–	–	8.87E-04	0.0018	8.8E-04	0.0018
lead ^	0.0012	0.0013	2.7E-04	5.1E-04	0.0015	0.0018
mercury * ^	3.7E-06	0.0014	–	–	3.7E-06	0.0014
methane	2.09	–	0.11	0.19	2.19	0.19
nitrogen oxides *	3.42	3.59	37.8	69.7	41.2	73.3
odorous sulfur	0.0051	0.054	–	–	0.0051	0.0054
other organics *	0.072	0.073	3.09	3.25	3.16	3.33
particulates *	1.45	1.39	11.5	25.4	13.0	26.8
propylene $	–	0.92	–	–	–	0.92
propylene chlorohydrin$	–	0.034	–	–	–	0.034
propylene oxide $	–	2.07	–	–	–	2.07
sulfur oxides *	4.17	4.37	30.7	66.9	34.8	71.3

* Emission results from acquisition and fuel combustion; mat'ls w/o designation were process-related wastes

^ Emission results from production of sodium hydroxide and chlorine utilized in paper manufacturing

Emission results from EG process only

$ Emission results from PG process only

NOTE: • Dilution ratios are 53% PG product/47% water and 50% EG product/50% water
  • Data do not include atmospheric emissions associated with combustion of solid waste or post-consumer emissions (55)

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[8]These data assume that post-consumer atmospheric emissions are negligible for the following reasons: (1) exposed, undiluted PG and EG antifreeze solutions did not generate atmospheric emissions at 65˚F, and (2) atmospheric emissions from leaking of antifreeze solution are negligible because EG/PG solution are enclosed within internal combustion engines (55).

TABLE 17: Industrial Waterborne Emissions Associated with Production of 1,000 Gallons of EG- and PG-Based Antifreeze Solutions (55)

	Process EG (lbs.)	Process PG (lbs.)	Fuel EG (lbs.)	Fuel PG (lbs.)	Total EG (lbs.)	Total PG (lbs.)
acid*	0.37 lbs	44.2 lbs	2.03 lbs	4.53 lbs	2.40 lbs	48.7 lbs
ammonia	0.0015	0.0016	–	–	0.0015	0.0016
biological oxygen demand	0.56	0.59	0.035	0.068	0.60	0.66
chromium	1.4E-04	1.5E-04	–	–	1.4E-04	1.5E-04
chemical oxygen demand	0.63	0.66	0.098	0.19	0.73	0.85
cyanide	1.6E-06	1.6E-06	–	–	1.6E-06	1.6E-06
dissolved solids *	9.56	19.6	13.9	25	23.5	44.6
fluorides	8.5E-05	9.0E-05	–	–	8.5E-05	9.0E-05
herbicides !	1.7E05	1.8E-05	–	–	1.7E-05	1.8E-05
hydrocarbons ##	–	4.07	–	–	–	4.07
iron *	4.1E-06	4.4E-06	1.6	3.3	1.6	3.30
lead ^	5.5E-09	2.1E-06	–	–	5.5E-09	2.1E-06
mercury ^	1.0E-08	3.8E-06	–	–	1.0E-08	3.8E-06
metal ion *	3.5E-05	3.8E-05	0.51	1.14	0.51	1.14
nickel	5.5E-09	2.1E-06	–	–	5.5E-09	2.1E-06
nitrogen !	0.002	0.002	–	–	0.0020	0.0021
oil	0.23	0.024	0.018	0.034	0.25	0.27
pesticide !	8.6E-06	9.1E-06	–	–	8.6E-06	9.1E-06
phenol*	7.7E-05	5.87	0.0089	0.017	0.0089	5.89
phosphates	0.019	0.02	–	–	0.019	0.020
sodium hydroxide	–	6.27	–	–	–	6.27
sulfides	0.17	0.18	0.0089	0.017	0.18	0.19
sulfuric acid *	–	–	0.019	0.039	0.019	0.039
suspended solids	2.26	0.75	0.053	0.1	2.31	0.85
zinc	0.0031	0.0032	–	–	0.0031	0.0032

  * Emission results from acquisition and fuel combustion; materials w/o designation were process-related wastes

  ^ Emission results from production of sodium hydroxide and chlorine utilized in paper manufacturing

  # Emission results from EG process only

  $ Emission results from PG process only

  ! Emission results from production of starch utilized in adhesive for corrugated cardboard containers

 ## Emission results from heavy ends of separation columns for producing PO; not analyzed for specific chemical composition

NOTE: • Dilution ratios are 53% PG product/47% water and 50% EG product/50% water
         • Sludges from in-house or POTW waste water treatment are accounted for in data

(3) Disposal Scenarios for Spent Antifreeze Solution

Figure 5 is a description of the post-production waste management and recycling scenarios for spent antifreeze considered in the FAL study. The disposal scenarios include kiln incineration, waste water treatment, deep-well injection, and improper disposal (ground, storm sewers, and landfilling) (55). FAL assumes that "proper" disposal methods process spent antifreeze solutions to a point in where they are not harmful to the environment (55). This assumption seems inappropriate given that deep well injection, wastewater treatment, and all types of waste combustion result in environmental emissions. FAL states that such emissions are negligible in terms of the overall waste produced by this product system. However, ambient emissions associated with all waste disposal methods have inherent impacts on human and ecological health, as well as sociological impacts on the communities in which it occurs. It is therefore misleading to assume that chemical waste product can be managed to a point where it is entirely "benign."

Table 18 describes the waterborne chemical wastes that are generated through improper disposal of spent antifreeze product. Data are provided for PG solutions with dilution ratios of 50/50 and 53/47. Improper disposal means dumping of spent antifreeze on the ground, into storm sewers, or directly into a body of water without application of treatment measures. These data assume that 39% of all antifreeze consumed is disposed of improperly (56).

The dilution ratio for PG has a significant impact on the resulting waterborne wastes associated with improper disposal of 1,000 gallons of antifreeze solution. By decreasing the dilution ratio by 6% the resulting total waste for the PG solution decreased from 1731.27 lbs. to 1633.62 lbs., as compared to 1,692 lbs. for the EG solution. Specifically, the glycol component of the PG product is lowered from 1,681 lbs. to 1,586 lbs., as compared to 1,665 lbs. for the EG solution. Both EG and PG solutions had similar inhibitor contents, with exception to sodium tetraborate (12.1 lbs. and 34.1 lbs., respectively). In summary, consideration of these data using equivalent dilution ratios (50/50) results in the total amount of improperly disposed waterborne waste associated with the PG solution to be less than the EG solution.

Figure 5: **Post-Production End Use, Waste Management, and Recycling Scenarios for EG- and PG-Based Spent Antifreeze Solutions**
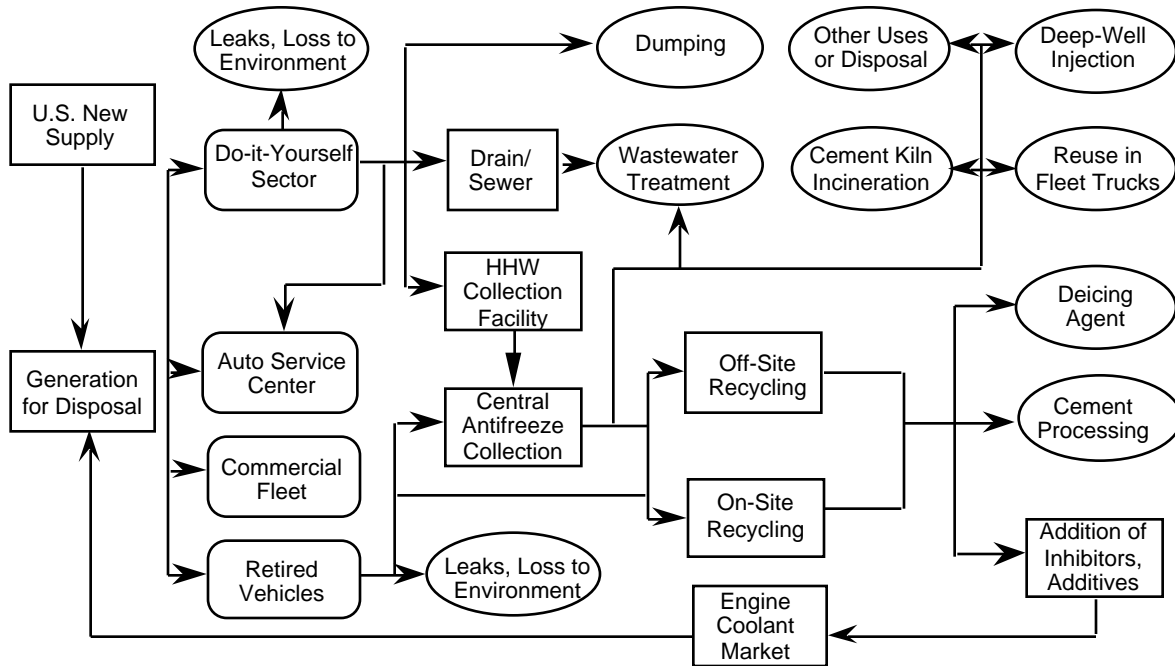

TABLE 18: **Waterborne Wastes Generated by Improper Disposal of 1,000 gallons of EG- and PG-Based Antifreeze Solutions (55)**

	lbs. EG*	lbs. PG*	lbs. PG**
Ethylene Glycol	1,665.000	0	0
Propylene Glycol	0	1,586.000	1,681.000
Sodium Hydroxide	3.810	3.540	3.710
Sodium Nitrate	2.420	5.060	5.400
Sodium Orthophosphate	5.190	0	0
Sodium Silicate	3.810	4.900	5.060
Sodium Tetraborate	12.100	34.100	36.100
Lead***	0.016	0.016	0.016
TOTAL	**1692.340**	**1,633.620**	**1,731.270**

Note: *   Dilution ratio is 50% antifreeze product / 50% water

   **   Dilution ratio is 53% antifreeze product / 46% water

   ***   Lead is not present if antifreeze product is dumped in unused form

Spent antifreeze solutions (post consumer solid waste) must be treated as a potential hazardous waste under the Resource Conservation and Recovery Act[9] (RCRA). Generators of large quantities of spent antifreeze must test this material for toxicity characteristics (40 CFR 261.24). Generally the lead content of spent antifreeze solutions results in the "hazardous" designation (5 ppm or greater)[10]. The lead is derived from corrosion of solder used to seal engine radiators. (56, 68). Bench-scale tests indicate that PG-based antifreeze solutions may corrode high-lead solder less than the EG equivalent (68). This suggests that spent antifreeze solutions containing PG are less likely to be designated as a "hazardous waste." However, additional data regarding corrosion protection are needed to validate this hypothesis.

(4) Recycling and Reuse Scenarios for Spent Antifreeze Solution

Figure 5 depicts the various end-use options for production and disposition of recycled antifreeze. (Appendix F of the FAL study describes antifreeze recycling programs, but this information is not available for inclusion in the case study.)

Sources of spent antifreeze includes auto dealerships, service stations, truck and automotive fleet operations, and utility companies. The latter source utilizes EG and PG as a heat exchange fluid in large quantities (72). FAL considers house-hold hazardous waste collection as a potential source. However, many antifreeze recyclers do not accept household collections due to contamination concerns (74). Many communities do not accept antifreeze at household hazardous waste collec-tions due to the sheer volume of the material. People are encouraged to take the material to automotive service stations, who either accept the material for free or at a minimal charge ($0.25/gallon) (74, 75). General Motors Corporation has im-plemented a formal antifreeze recycling program at its dealerships in the U.S. (73).

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[9]Recently the EPA was petitioned to include spent antifreeze in its proposed "Universal Waste Rule" (58 FR 8102). Inclusion of EG and PG antifreeze solutions in this rule would have designated spent antifreeze with a generic "non-hazardous listing" under the RCRA. It would have allowed this material to be handled under less stringent provisions involving no manifests or complex permitting. However, this rule would not have eliminated requirements for proper disposal as a solid waste under RCRA (55). On May 11, 1995 this petition was rejected by the current EPA administrator (60 FR 25492).

[10]EPA's extraction procedure (EP) and toxicity characteristic leachate procedure (TCLP) tests the amount of extractable levels of heavy metals, rather than the total concentration in solution. These tests are utilized to determine the likelihood that a potential hazardous waste will release heavy metals into ground water and pollute drinking water. (73)

Prior to accepting a load of spent antifreeze, recycling companies sample and test the material for pH, reserve alkalinity, and freezing point. Solutions that have a gas or solvent-like odor or contain excessive oils are rejected (73, 74). Transport and storage requirements associated with hazardous wastes must also be followed by antifreeze recycling companies. Mal Hickok of Recycling Fluid Technology, located in Battle Creek, Michigan, notes that EG and PG are mixed quite commonly in their processing operation. This is not a problem for recyclers because the percentage of PG-based antifreeze is still quite small. Hickok indicates that if PG use increases technology and/or collection procedures may have to be adjusted in order to maintain a marketable reuse product (74).

Research indicates that PG and EG antifreeze re-processing technology is quite effective and is a rapidly growing facet of the chemical recycling market (73, 74, 75). Current recycling technology includes but is not limited to the following processes: (1) simple filtration; (2) filtration and flocculation/coagulation; (3) filtration, coagulation/flocculation, air oxidation (with and without deionization); (4) deionization; (5) reverse osmosis; 6) filtration, centrifugation, multiple inhibitors, with and without deionization; (7) vacuum distillation; and (8) coolant life extension (73).

RFT's reprocessing consists of a pre-cleaning stage, a membrane filtration process, and the addition of an inhibitor package formulated by Dow Chemical or Penray. The end-use of the recycled antifreeze solution determines which inhibitor package is chosen (74). Their operation results in negligible air pollution emissions. However, distillation and other processes used in recycling operations produces air pollution discharges high enough to require federal and/or state permits (74). Research also indicates that the current recycling technology utilizes significant energy consumption (74, 75). In addition, the material filtered by membrane processes must be tested to determine if it exhibits the characteristics of hazardous wastes (74).

The negative characteristics of spent antifreeze solutions addressed during the reformulation process include the formation and accumulation of EG degraded acids (i.e., acetic, glycolic, and formic), dissolved and suspended solids (principally metal oxides and salts corroded within coolant system), and make-up water contaminants (73). Studies indicate that the chemical, physical, and performance requirements of virgin antifreeze solutions can be met with the recycled equivalent given present technology and the addition of an adequate chemical inhibitor package (72, 73). Reuse options for spent antifreeze include fleet truck engine

coolants, deicing agents for planes, additives for cement processing, and auto-motive engine coolants (55).

RFT sells its their pre-mixed recycled antifreeze product at $2.25/gallon. They do not charge their customers a disposal fee ($0.50/gallon) if they re-purchase equal volumes of the recycled product (74). The public and industry tends to perceive recycled antifreeze as an inferior product, without significant cost savings to customers. Hickok indicates that this perception is the result of early recycling operations, whose products were discolored and had solvent-like odors. A higher quality product and increasingly stringent disposal regulations seems to be increasing the acceptance of use of recycled antifreeze solutions (73, 74).

H. Properties of Reaction Inputs and Outputs

(1) Physical and Chemical Characteristics

Table 19 contains a list of physical and chemical properties of PG and EG reactions and reaction products. Due to limited available information this data applies only to end products (PG, EG) and chemical intermediates, (EO, PO, and *tert*-butyl hydroperoxide). These data do not reflect specific production processes utilized by industry today and are not compatible with data presented by FAL. Thus, the information in Table 19 should be considered theoretical in nature unless verified independently.

The available information in the literature is not sufficient to make comparisons of atom economy and reaction yield. The percent selectivity for formation of EG and PG is equivalent (90%) because they are produced using similar hydrolysis reactions. Although both EO and PO reactions have equivalent selectivities, their percent feedstock conversions differ significantly (7–15% vs. 98%, respectively). When the 48% conversion factor for the initial TBH reaction of PO production is accounted, the resulting conversion factor is 47% for the overall PO reaction. This is still between three and six times higher than that of the EO reaction.

TABLE 19: **Physical and Chemical Properties of Feedstock Chemicals Used in Production of EG- and PG-Based Antifreeze Products (66, 67, 68, 69, 71)**

	EG	PG	EO	PO	TBH
REACTION PROPERTIES					
Rxn Temperature (˚C)	200	125–200	220–275	110–120	120–140
Rxn Pressure (MPa)	n/a	2	1–2.2	4	3.63–5.0
% Feedstock Conversion	n/a	n/a	7–15	98 (9%/pass)	48
% Selectivity	90	~ 90	80	80	50
PRODUCT PROPERTIES					
Boiling Point@101.3 kPa (˚C)	197.6, 107*	187.9, 104.5*	10.8	34.23	n/a
Freezing Point (˚C)*	-36.67	-33.33	n/a	n/a	n/a
Vapor Pressure (Pa)	300@65˚C	11@20˚C	145.6@20˚C	58.8@20˚C	n/a
LEL (vol %)	3.20	2.6	2.6	2.3	n/a
UEL (vol %)	53	n/a	100	36	n/a
Ignition Temperature (˚C)	410	410	429	430	n/a
Flash Point (˚C)	111	103	n/a	-37	n/a

NOTE: • PO is produced via hydroperoxidation of isobutane

• EO is produced via oxidation of ethylene with oxygen (>99% pure)

• PG and EG produced via hydrolysis of PO and EO, respectively

• TBH = *tert*-butyl hydroperoxide

• LEL = lower explosive limit; UEL = upper explosive limit

• n/a designates data which is not available for comparison

• (*) Data applies to antifreeze solutions with ratio of 50% water/50% glycol component

Safety issues associated with storage and transportation of the chemicals mentioned in Table 19 are also important factors. Both EG and PG are transported by rail tank car, tank truck, or ship. A nitrogen blanket is employed to prevent oxidation of glycols. Both compounds are stable and non-corrosive in nature (66, 68). EO and PO are highly flammable, explosive compounds. It is important that storage and transport vessels are free of impurities which may cause rapid polymerization. EO and PO are transported by ship, railcar, and tank truck (71, 72). Many EO and EG production facilities are located adjacent to one another (67).

(2) Toxicity and Health Effects

Table 20 describes the prominent toxicity and health effects associated with
exposure to EG, PG, EO and PO chemicals, but not necessarily antifreeze products
or solutions. These data represent a cursory review of toxicity literature and
should be utilized cautiously for making general comparisons. Although not
considered in this case study, the other determinants of antifreeze toxicity are the
anti-corrosive and glycol anti-oxidizing agents[11]. Both EO and PO have similar
acute effects, however, the latter has a higher minimum oral toxicity in rats (300
g/Kg versus 0.33 g/Kg, respectively). Both chemicals have carcinogenic potential
and other potential chronic health effects.

**TABLE 20:   Toxicity and Adverse Health Effects Associated With
            EG, PG, EO, and PO (66, 67, 68,69, 71)**

	EG	PG	EO	PO
Acute Health Effects	narcosis, kidney damage	little to none	headaches, nausea, vomiting, numbness	headache, skin and respiratory irritation
Acute Oral Toxicity (LD$_{50}$)	1.56 g/Kg (adult)	20 g/Kg	0.33 g/Kg (adult)	300–1000 g/Kg (rats) (rats)
Chronic Health Effects	kidney damage	none reported	sensory-motor neuropathy	CNS depression
Lethal Dose (Adult)	0.1 L	1 L	n/a	n/a
Evidence of Teratogenicity	yes (mice, rats)	none reported (mice, rats, rabbits)	none reported in rats	none reported
Evidence of Carcinogenicity	none reported	none reported	yes$	yes#

NOTE: $ EO is classified by the American Conference of Governmental Industrial Hygienists
            (ACGIH) as an A2 suspected human carcinogen

    #   PO is classified by EPA as a probable human carcinogen (B-2 substance) and by the
        International Agency for Research on Cancer (IARC) as a 2A carcinogen

    n/a Indicates data are not available through literature review

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[11]Arsenical compounds were once utilized as an anti-corrosive agent in antifreeze solutions (66)

The principal argument of PG-based antifreeze product manufacturers is that their product has a very low acute toxicity and is therefore a much safer alternative than the EG counterpart. The lethal oral dose of EG (0.1 L) is a factor of ten smaller than PG (1 L) for adults. EG has a sweet taste and odor, making consumption particularly attractive by animals and small children (67, 68). Indeed, EG-based antifreeze ingestion is one of the most commonly reported poisoning problem with dogs and cats. The Illinois Animal Poison Information Center (reports 106 cases of EG poisonings in that state in 1988 (68). The Colorado State University Veterinary Teaching Hospital reports EG-based antifreeze intoxication in cats and dogs as the cause of 50% of all deaths due to poisonings between 1979 and 1986 (68).

The U.S. Food and Drug Administration (FDA) classifies PG as "Generally Regarded as Safe" (GRAS)[12] (68). It is an allowable ingredient at specific concentrations in alcoholic beverages, confections and frostings, pet foods, frozen dairy products, seasonings and flavors, nuts and nut products, other food categories (68). PG is often administered as an antidote to EG poisoning victims because it prevents metabolism of EG into oxalic and glycolic acids. These compounds mediate pH changes in the blood, leading to acidosis and potentially life-threatening kidney damage. PG is excreted unchanged into the urine and metabolized into lactic and pyruvic acids (68, 76).

An important aspect of discussing toxicity and health effects is the exposure potential of the person(s) or organism(s) at risk. Certainly there is occupational exposure potential for all chemicals associated with the production of the compounds contained in Table 20, as well as others utilized in production. Both EG and PG antifreeze solutions provide little inhalation potential at room temperature due to their low vapor pressure. The temperature of internal combustion engines (~148.9˚C) may cause the formation of inhalable vapors. However, engine coolant systems are enclosed during operation. A leaky coolant system must be operated for an extended period of time in an enclosed, unventilated space before significant glycol vapor formation is likely to occur. This may be potential accidental exposure scenario for autoservice station attendants.

Automobile mechanics change engine coolants in the following manner: (1) drain the coolant into pan while the engine is not in operation, (2) add pure water to engine coolant system while engine is operating, (3) drain remaining

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[12]The GRAS designation for PG was made by FDA in 1977 after a formal review of available toxicity literature from 1920 to 1970 (68).

solution from engine coolant system while engine is off, and (4) add new glycol solution to engine coolant system. Some automotive service centers have completely enclosed systems that eliminate manual filling and draining steps. Both situations present minimal acute exposure potential due to lack of vapor formation. However, additional research is necessary to provide definitive evaluations of potential acute and chronic exposures.

(3) Feedstock Purity

The purity of feedstock chemicals is another important consideration which have implications for chemical performance and reaction efficiency. There are two commercial grades of PG, a high purity industrial grade and a higher-purity, "super pure" or "USP" grade. Only the USP grade is utilized for pharmaceuticals, cosmetics, and food additives (69). The directly synthesized EG product (fiber grade) is greater than 99.8% pure, while the lower quality antifreeze grade have a purity rating of less than 98.0%. Antifreeze grade can be recycled from waste water produced during EO production (67).

PO from chlorohydrin, tert-butyl, or ethylbenzene production processes all have purity ratings of 99.9%. The quality of the propylene feed contributes significantly to the impurity content of the final product. Polymer grade propylene is preferable to reduce formation of acetaldehyde and EO in the reactor vessel. Additional impurities may be present in production processes (i.e., chlorinated organic compounds, hydrocarbons, ethers, aldehydes, acetone, methanol, butanol, and *tert*-butyl alcohol or furan). EO is obtained at consistently high purity irrespective of production process with a minimum concentration of 99.5% (71, 72).

(4) Performance Criteria

Table 21 is a list of performance-oriented properties for PG and EG antifreeze solutions, along with the applicable American Society of Testing and Measurement (ASTM) testing method (68). Antifreeze specifications and performance requirements are determined by three major purchasing groups: vehicle manufacturers, consumers, and government agencies (66). All major auto manufacturers have antifreeze specifications for their automobiles, which depend on the location of vehicle use and age of vehicle. The General Services Administration, as well as branches of the U.S. military have performance-based specifications for antifreeze used in its fleet vehicles. Some states require antifreeze specifications and other aspects regarding sale and distribution be recorded into law (66).

TABLE 21: **ASTM Testing Methods for Performance Properties of EG- and PG-Based Antifreeze Solutions (68)**

Property	ASTM Test Method
Freezing Point (Fp)	D1177, D3321
Boiling Point (Bp)	D1120
Specific Gravity	D1122
pH[1]	D1287
Reserve Alkalinity[1]	D1121
Foaming Dependency	D1881
Ash Content[1]	D1119
Effect on Finishes	D1882

NOTE: [1]Solution pH, reserve alkalinity (buffer capacity), and ash content are all gross measures of corrosion inhibitor levels

The freezing points for 50/50 dilute antifreeze solutions are -36.6°C (EG) and -33.3°C (PG). The boiling points of 50/50 dilute antifreeze solutions are 107°C (EG) and 104.5°C (PG). Research indicates that these differences are within ASTM's allowable error of measurement (68, 77). Geographic location of use will most likely determine whether or not the few degrees of freeze and boil over protection are important advantage to the consumer.

Corrosion inhibitors added to PG- and EG-based antifreeze solutions hinder the oxidation of these compounds to corrosive derivatives (66). Coolant corrosivity is a function of the glycol base, engine materials, nature of heat rejection surfaces, water quality (chloride content), and cooling system temperatures (66). Formulations with low corrosiveness for EG antifreeze solutions include phosphates, benzoates, sebacates, borates, nitrates, silicates, molybdates, or other organic compounds (amines, benzotriazoles, orimidazoles) (66). Inhibitor formulations vary between manufacturers and country of use, which may result in different physical and chemical properties.

Bench scale and limited road tests suggest that PG-based coolants may have greater protection against cast iron and cast aluminum cavitation corrosion (68). Cavitation corrosion results from formation of vapor bubbles in engine coolant solutions. Vibration of the engine causes these bubbles to "collapse" violently producing localized stress estimated at 60,000 psi. Several US heavy duty engine manufacturers recommend use of PG-based solutions. Tests by Cummins on four different engines resulted in adequate performance of PG-based coolants for

over 400,000 miles per engine. Detroit Diesel, an engine manufacturer formally owned by General Motors Corporation, approves PG use in its 40, 50, and 60 series diesel engines because it causes less engine cavitation corrosion (68).

I. Reaction Economics

Appendix 4 contains the raw material, utility, and other production costs associated with the production of EG, PG, EO, and PO(78). These data apply to EG and PG produced by non-catalytic liquid phase hydration of EO and PO, respectively, at the specified conditions. Data regarding EO includes production via air and oxygen oxidation methods. Data regarding PO includes production via chlorohydrination, isobutane hydroperoxidation, and ethylbenzene hydroperoxidation.

PG plant gate costs (net production cost minus general/administrative, sales, and research expenses) are slightly higher than that of EG at a 400-million-pound annual production capacity ($0.67/lb vs. $0.53/lb, respectively). This difference in production costs seems to be a factor of the difference in the raw materials costs (PO = $0.756/lb., EO = $0.58/lb.). This seems to be tempered by PG's higher byproduct credits (PO = $0.097/lb., EO = $0.055/lb.) and lower utility expenses (PO = $0.027/lb., EO = $0.033/lb.). Most of the other production costs are similar for these processes (78).

The data regarding EG and PG production do not specify which processes are used in producing EO and PO feedstocks. More than likely, production costs are going to vary between these alternative production processes. PO plant gate costs for the conventional chlorohydrin, T-butanol (ARCO), and styrene (ARCO) process are as follows: $0.55/lb, $0.23/lb, and $0.40/lb (annual production capacity = 400 million pounds), respectively. For EO, plant gate costs for air and oxygen oxidation processes are $0.44/lb and $0.40/lb, respectively (annual production capacity of 300 million pounds) (78). The variation in the production capacities is not expected to have a significant affect if data were normalized. However, the production process does seem to affect the production costs of PG and EG antifreeze solutions.

In summary, the usefulness of these data are limited because actual production costs of the complete PG and EG antifreeze solutions, including the additional formulation chemicals, are not included. Information regarding less tangible, hidden, and liability costs associated with the production and use of EG- and PG-based antifreeze solutions is not available at this time. Additional information regarding costs to consumers would also provide a more detailed comparison.

J. Regulatory Requirements

Several European countries restrict or ban use of EG-based antifreeze solutions due to their acute toxicity. Examples include the Swiss Poison Control Law (1974) and a 1989 Austrian regulation, which ban retail sale of EG-based antifreezes. In addition, public transit and automotive maintenance unions in West Germany, Denmark, and other countries have made formal demands for the removal of EG-based products from their workplaces (68).

The U.S. has no federal restrictions on the use of either PG or EG antifreezes, although existing regulations specify packaging, labeling, and registration requirements. Oregon requires all EG antifreezes sold within its jurisdiction to contain a bittering agent to deter consumption by animals and small children (68). Several municipalities have passed similar laws, which has resulted in the standardization of this practice by many of the large EG antifreeze formulation companies (19). Producers have also instituted child-resistant enclosures, warning labels, and consumer awareness programs to reduce fatal accidental poisonings (75). Many states have also established antifreeze compounds registrations that include minimum performance characteristics (66).

The following federal environmental statutes regulate EG as an air, water, and soil pollutant: 1990 Clean Air Act Amendments (EG designated as a "hazardous air pollutant" [HAP] - 42 USC § 7412(b)), CERCLA - (EG designated as "hazardous substance" - HAPs under 42 USC § 7412(b) are incorporated into 42 USC § 9601(14)), Superfund Amendments and Reauthorization Act (SARA) Title III (EG designated as "toxic chemical" - 42 CFR § 372.65), and Safe Drinking Water Act (health advisory has been issued for EG in drinking water).

Finally, spent antifreeze that meets RCRA-specified toxicity levels must be managed and disposed of by licensed hazardous waste transporters and disposal facilities. This is not necessarily true of all generators of spent antifreeze, however. Generator management and disposal requirements depend on quantity produced each month. RCRA considers firms producing less than 100 kg of hazardous spent antifreeze per month conditionally small-quantity generators. Although responsible management procedures must always be followed, these regulations do not require the manifesting procedures of larger-quantity generators. However, RCRA regulations vary between states and may be more stringent than federal requirements. For "do-it-yourselfers," this constitutes disposal at a local household hazwaste drop-off facility or auto service center. Commercial facilities must pay licensed hazardous waste haulers to remove spent antifreeze from their property.

K. Discussion of Data Interpretation

This case study demonstrates that numerous trade-offs become apparent when performing chemical life cycle analyses. The data presented in the various categories make it difficult to distinguish EG and PG-based antifreeze products as a more advantageous chemical or reaction pathway. Positive characteristics associated with production and use of the EG-based antifreeze solution include reduced solid waste generation, total atmospheric and waterborne emissions, and energy consumption. In addition, the EG-based solution has slightly higher freeze and boil-over protection. The PG-based alternative has the advantage of lower end-use toxicity and reduced internal engine corrosion potential. However, the validity of these generalizations is limited by a number of issues related to data collection and presentation. Additional data regarding production costs, regulatory compliance, spent antifreeze recycling, wastes associated with improper disposal, and feedstock quantification are necessary to differentiate the two alternatives in these categories.

One of the major challenges associated with developing a case study of this nature is defining reaction pathways. Ideally, comparisons drawn from chemical life cycle analyses are consistently based on defined reaction parameters, as specified in Figure 3. When one considers the capacity and highly specialized nature of industrial chemical production facilities, slight variations in any one of these parameters has a profound influence on the output in all other aspects of reaction systems. For example, the choice between highly pure oxygen and air as an oxidizing agent in EO production results in a 13% difference in feedstock conversion and a 5% difference reaction yield (71). Such differences in reaction efficiency affect production costs, environmental emissions, production of reaction residuals, and the amount of required feedstocks and other reaction inputs.

The initial data collection strategy for this case study was to utilize the EG and PG reaction parameters defined in the FAL study as a guide for accumulating quantitative and qualitative data for all other categories. The competitive nature of the chemical industry limited the willingness of FAL and its sponsor, Union Carbide Corp., from disclosing the appendices which contains this information.

The production databases and reference texts that provide data regarding reaction conditions, reaction efficiency, processing technology, catalysts, and reaction medium are not necessarily consistent with those utilized by FAL in its study. In addition, these sources do not necessarily reflect current production technology. Such potential inconsistencies reduces the value of comparisons that

draw upon FAL data (i.e., industrial environmental emissions, energy consumption and reaction residuals) and non-FAL data (i.e., reaction economics) as well as those within specific data categories (i.e., feedstock, product, and packaging systems).

A factor that contributes to this data consistency problem is the presentation of all PG data in terms of a weighted-average of the three major production processes for PO. Such aggregation does not account for significant differences in the three different PO processes. In the case of air and waterborne industrial emissions, entire categories of pollutants accounted for in the FAL study may be eliminated if the analyses are limited to one of the PO production process. This data averaging procedure seems even less appropriate given that the higher energy consumption of the entire PG reaction system is linked to PO production (55).

Consideration of one PO reaction step would have resulted in more equivalent comparison of the EG and PG reaction systems. It also would have facilitated the identification of applicable reaction cost data and more accurate calculation of feedstocks documented in Appendix 5. An even more useful strategy would be to incorporate evaluation of the three PO reactions independent of one another. This would have facilitated integration of data from multiple sources, providing greater potential consistency of all data used in the analyses. In addition, it would have provided the greatest opportunity to identify areas of improvement in the PG product life cycle.

The use of alternate dilution ratios for PG-based antifreeze solution is another complicating factor of this case study. Sensitivity analysis indicates that feedstock and other reactant quantities, product packaging, post consumer solid waste, and atmospheric and waterborne emissions associated with the PG reaction system are reduced to levels comparable to those in the EG reaction system when the antifreeze dilution ratios are decreased from 53% to 50% antifreeze product. A profound difference in the quantity of the improperly disposed PG-based spent antifreeze solutions is also noted. Such normalization calculations provide a "level playing field" for comparison of the EG and PG antifreeze solutions. However, they are not necessarily appropriate because consumer behavior and preference, rather than product performance, may have a greater influence on product use scenarios.

L. Conclusions and Recommendations

This case study demonstrates the application of multi-disciplinary evaluation criteria for comparing alternative chemicals and reaction pathways. It also

illustrates the value of the "life cycle" perspective in identifying production and use trade-offs associated with such analyses. Indeed, the significance of such competing concerns is potentially biased by needs and values of individual chemists, and quite very often their employers. However, utilization of the complex evaluatory criteria applied in this case study will challenge these individuals to expand their decision-logic, resulting in more informed comparisons of chemicals and reaction pathways. The importance of this work lies in the development of a methodology to facilitate collection and presentation of chemical life cycle data in a consistent and least biased manner. It represents a "first step" in incorporating a more environmentally conscious decision-making methodology into the underlying evaluation processes of future chemists.

Recommendations are suggested to overcome the aforementioned limitations of this case study, enhance the value of chemical life cycle comparisons, and facilitate incorporation of such analyses into university-level chemical science curricula. First, more specific guidelines for defining and applying chemical reaction systems in life cycle analyses are necessary to legitimize their scientific value. Standardizing the type and manner in which reaction parameters are presented in chemical life cycle analyses will minimize potential data misrepresentations and strengthen the scientific validity of life cycle analyses. Practitioners may chose to focus on the following related issues: 1) guidelines for use of proprietary information that ensure patent protection, and 2) flexible data collection and interpretation methodologies which are designed to accommodate reactions of varying complexities.

Consumers and other individuals generally do not understand the complexities and assumptions associated with chemical life cycle analyses. This presents an opportunity for organizations to make superficial claims regarding energy, residuals, and performance which may be scientifically unjustified. Formal methods to consistently define reaction parameters may therefore discourage subjective assessments of data, such as the following statement from a Union Carbide news release:

> The Franklin study demonstrates that, on virtually every environmental basis reviewed, traditional ethylene glycol antifreeze solutions in the leading brands have less potential environmental impact than the solution alleged to be environmentally "safer" (79).

Leadership in promoting standardized guidelines for defining chemical reaction parameters in chemical life cycle analyses should come from chemists and life cycle practitioners in industry, government, and academia. Involvement of these various stakeholders is necessary to develop support and promote use of the refined methodologies. Inclusion of federal regulators in these activities is desirable, although a federal regulatory policy may not be appropriate nor feasible[13]. Consensus building organizations, such as the International Standards Organization (ISO), Society for Environmental Toxicology and Chemistry (SETAC), and the American Chemical Society (ACS), may be appropriate vehicles to initiate this process.

To facilitate incorporation of life cycle "thinking" into chemical science curricula a streamlined methodology will be necessary to accommodate students and educators. Detailed and accurate data collection methodologies are an important aspect of minimizing potential biases associated with life cycle analyses. However, the technical expertise, time, and funding necessary to present formal life cycle analyses are not necessarily realistic for a classroom environment.

Academic and industrial chemists, as well as life cycle practitioners must work together to develop a refined teaching methodology for chemical life cycle analyses, and they must identify opportunities for inclusion in classroom activities. Future educational development efforts should include the use of chemical design software that incorporates multi-disciplinary evaluation criteria into their decision logic. Educators may also focus on the development of alternative laboratory experiments, problem sets, text-book supplements, and other curriculum development tools to integrate the relevant concepts into all levels of chemical science education. In addition, semester-long projects and discussion groups could provide a forum for integration of life cycle principles along side the traditional chemistry curriculum. Such projects could initially focus on simple, non-proprietary reactions to promote an understanding of analytical concepts. More advanced analytical exercises should challenge students to present life cycle comparisons given complex reactions, proprietary data, and limited reaction parameters. The goal of such efforts should be to provide chemistry students with the skill necessary to participate in data collection and interpretation activities associated with complex life cycle studies.

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[13]Section 503 of Executive Order No. 12873 (58 FR 54911, October 22, 1994) requires the EPA to establish generic guidelines for environmentally preferable products purchased and used by the federal government.