

**EMISSION FACTOR  
DOCUMENTATION FOR  
AP-42 SECTION 1.5  
LIQUEFIED PETROLEUM GAS COMBUSTION**

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# TABLE OF CONTENTS

	<u>Page</u>
LIST OF TABLES.....	v
CHAPTER 1. INTRODUCTION.....	1-1
CHAPTER 2. INDUSTRY DESCRIPTION.....	2-1
2.1 CHARACTERIZATION OF THE INDUSTRY.....	2-1
2.2 PROCESS DESCRIPTION.....	2-2
2.3 EMISSIONS.....	2-2
2.3.1 Nitrogen Oxides Emissions.....	2-2
2.3.2 Carbon Monoxide Emissions.....	2-3
2.3.3 Sulfur Oxides Emissions.....	2-4
2.3.4 Particulate Matter Emissions.....	2-4
2.3.5 Organic Compound Emissions.....	2-5
2.3.6 Trace Element Emissions.....	2-6
2.3.7 Carbon Dioxide Emissions.....	2-6
2.3.8 Nitrous Oxide Emissions.....	2-6
2.3.9 Fugitive Emissions.....	2-7
2.4 CONTROL TECHNOLOGIES.....	2-7
REFERENCES.....	2-10
CHAPTER 3. GENERAL DATA REVIEW AND ANALYSIS PROCEDURES.....	3-1
3.1 CRITERIA POLLUTANTS.....	3-1
3.1.1 Literature Search .....	3-1
3.1.2 Literature Evaluation.....	3-3
3.2 NON-CRITERIA POLLUTANTS.....	3-4

3.3 FUGITIVE EMISSIONS.....	3-4
REFERENCES.....	3-6
CHAPTER 4. EMISSION FACTOR DEVELOPMENT.....	4-1
4.1 CRITERIA POLLUTANTS.....	4-2
4.1.1 Review of Previous Data.....	4-2
4.1.2 Review of New Data.....	4-2
4.1.3 Compilation of Emission Factors.....	4-3
4.2 NON-CRITERIA POLLUTANTS.....	4-4
4.3 FUGITIVE EMISSIONS.....	4-4
REFERENCES.....	4-8
CHAPTER 5. AP-42 SECTION 1.5: LIQUIFIED PETROLEUM GAS COMBUSTION.....	5-1

TABLE OF CONTENTS (continued)

	<u>Page</u>
APPENDIX A. SAMPLE CALCULATIONS.....	A-1
APPENDIX B. MARKED-UP 1982 SECTION 1.5.....	B-1

## LIST OF TABLES

<u>Table</u>		<u>Page</u>
2-1	Comparison of LPG and Natural Gas Sales For 1989.....	2-9
4-1	Natural Gas Combustion Emission Factors.....	4-6
4-2	LPG Combustion Emission Factors.....	4-7
4-3	Fugitive Emission Factors For Various Equipment Types.....	4-7

## 1. INTRODUCTION

The document, "Compilation of Air Pollutant Emission Factors" (AP-42), has been published by the U.S. Environmental Protection Agency (EPA) since 1972. Supplements to AP-42 have been routinely published to add new emissions source categories and to update existing emission factors. An emission factor is an average value which relates the quantity (weight) of a pollutant emitted to a unit of activity of the source. The uses for the emission factors reported in AP-42 include:

- ! Estimates of area-wide emissions;
- ! Emission estimates for a specific facility; and
- ! Evaluation of emissions relative to ambient air quality.

The EPA routinely updates AP-42 in order to respond to new emission needs of State and local air pollution control programs, industry, as well as the Agency itself. Section 1.5 in AP-42, the subject of this Emission Factor Documentation (EFD) report, pertains to liquefied petroleum gas (LPG) combustion.

Section 1.5, Liquefied Petroleum Gas Combustion, was previously updated in 1982. The purpose of this current revision is to review and update, if possible, the prior emission factor development for criteria pollutants, and to add non-criteria emission species if any data exist. This update is part of a larger effort in which all sections of AP-42 are being revised. This emission factor document is part of the update effort. It provides background on the decision-making process for emission factor development, and documents the approach and results of the test data gathering effort.

The present update of AP-42 began with a review of the existing version of Section 1.5. The previous emission factors developed in 1982 were not based on LPG test data but were assumed to be the same as the natural gas emission factors on a

Btu thermal heat input basis (except for sulfur oxides which were based on fuel sulfur content). This default approach was adopted because of the lack of LPG data.

An extensive literature review was undertaken to identify and collect emissions data for LPG combustion for criteria and non-criteria pollutant emissions. The sparse amount of emissions data obtained were reviewed for quality as outlined in the draft EPA document, "Technical Procedures For Developing AP-42 Emission Factors And Preparing AP-42 Sections," (March 6, 1992).

Where data were located, the data reduction used the F-factor method specified in Reference Method 19 as contained in Appendix A of the Code of Federal Regulation Title 40 Part 60 (40 CFR). The lb/million Btu (lb/MMBtu) emissions rate calculated was then multiplied by the heating value for propane or butane (in MMBtu/thousand gallons) to produce an emission factor in terms of lb pollutant/thousand gallons. Analogous calculations were performed for metric unit emission factors.

Several new emission factors covering non-criteria pollutants have been added. These new emission factors pertain to total organic compounds (TOC), air toxics, and carbon dioxide (CO<sub>2</sub>). Information on control technologies for nitrogen oxides (NO<sub>x</sub>) emissions has been revised and updated.

Including the Introduction (Chapter 1), this EFD contains five chapters. Chapter 2 provides an overall characterization of LPG usage. The generic types of emissions are discussed together with general concepts for controlling NO<sub>x</sub> emissions generated from LPG combustion. Chapter 3 is a review of the emissions data collection and review procedures. The sources examined during the literature search are discussed and the emissions data rating procedures are defined. Chapter 4 details the development approach for new emission factors. It includes a review of specific data and the assumptions used to arrive at the final emission factors. Chapter 5 presents the revised AP-42 Section 1.5. Appendix A provides sample calculations for emission factor development.

## 2. INDUSTRY DESCRIPTION

This chapter contains a brief characterization of the LPG industry, and discusses LPG combustion processes, emissions and control options.

### 2.1 CHARACTERIZATION OF THE INDUSTRY

The term "LPG" in its broadest context refers to a group of refinery byproduct gases that may include the following compounds alone or in mixture: propane, propylene, butane, butylene, and isobutane<sup>1</sup>. Liquefied petroleum gas can be used for the same domestic, commercial and industrial applications as natural gas. One of the main LPG markets is in rural areas for domestic cooking and heating. The main advantage of LPG relative to natural gas is that, under pressure, it is a liquid which reduces transportation costs and makes long term storage practical. The main disadvantages are higher fuel costs and potential safety hazards in the event of leaks arising from the fact that LPG is heavier than air and may settle in explosive pockets in the absence of local air movement. Liquefied petroleum gas is also used in commercial and industrial applications as a standby fuel to replace natural gas during emergencies, or curtailments of baseline fuels. Recently, interest in LPG as a standby fuel has increased greatly in the South Coast Air Quality Management District (SCAQMD) in Southern California. The SCAQMD has mandated a phase out of oil as a stationary source fuel as part of ozone attainment plans. Natural gas is the primary alternative, but a noninterruptable supply cannot be assured, particularly during winter months. Accordingly, many boiler operators are installing capability for firing propane, butane or methanol.

Table 2-1 summarizes LPG sales to the residential, commercial and industrial sectors for 1989. Sales to the industrial sector are predominantly as chemical feedstocks.

## 2.2 PROCESS DESCRIPTION

The combustion processes that use LPG as a fuel are very similar to those that use natural gas. The use of LPG in commercial and industrial applications may require a vaporizer to provide the burner with the proper mix of air and fuel. An auxiliary vaporizer is used when the natural vaporization capacity of the LPG storage tank is not sufficient to meet the demand load of the burner(s) being served. The burner itself will usually have different fuel injector tips as well as different fuel-air ratio controller settings than natural gas since the LPG stoichiometric requirements are different than natural gas requirements. Liquefied petroleum gas is fired as a primary and backup fuel in small commercial and industrial boilers and space heating equipment. Liquefied petroleum gas can be used to generate heat and process steam for industrial facilities. Finally, LPG can be used in most domestic appliances that typically use natural gas.

## 2.3 EMISSIONS

The pollutants of primary concern from LPG combustion are the criteria pollutants:  $\text{NO}_x$ , carbon monoxide (CO), particulate matter (PM), sulfur oxides ( $\text{SO}_x$ ), and TOC. As a gaseous fuel, LPG does not produce a large amount of particulate emissions. The more significant emissions from LPG are the gaseous emissions.

### 2.3.1 Nitrogen Oxides Emissions

Nitrogen oxides are formed during combustion processes either as a result of thermal fixation of atmospheric nitrogen ( $\text{N}_2$ ) in the combustion air ("thermal  $\text{NO}_x$ "), or the conversion of chemically-bound nitrogen in the fuel ("fuel  $\text{NO}_x$ "). The term  $\text{NO}_x$  customarily refers to the composite of nitric oxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ). Nitrous oxide ( $\text{N}_2\text{O}$ ) is excluded from this definition of  $\text{NO}_x$ , but is an oxide of increasing interest as a greenhouse gas. Test data have shown that for most stationary combustion systems, more than 95 percent of the emitted  $\text{NO}_x$  is in the form of NO.

The qualitative global kinetics of thermal  $\text{NO}_x$  formation show that  $\text{NO}_x$  formation rates are exponentially dependent on temperature, and proportional to  $\text{N}_2$  concentration in the flame, the square root of oxygen ( $\text{O}_2$ ) concentration in the flame, and the residence time. Thus, the formation of thermal  $\text{NO}_x$  is affected by four factors: (1) peak temperature, (2)  $\text{N}_2$  concentration, (3)  $\text{O}_2$  concentration (or flame stoichiometry), and (4) time of exposure at peak temperature. The emission trends due to changes in these

factors are fairly consistent for all types of boilers -- an increase in flame temperature, N<sub>2</sub> availability, O<sub>2</sub> availability, and/or residence time at high temperatures leads to an increase in thermal NO<sub>x</sub> production regardless of the boiler type.

Fuel nitrogen conversion is only an important NO<sub>x</sub>-forming mechanism in oil and coal-fired combustion systems because of the high nitrogen content of these fuels. Nearly all NO<sub>x</sub> formed from LPG combustion is thermal NO<sub>x</sub>. A number of variables influence how much thermal NO<sub>x</sub> is formed with LPG combustion. The combustion chamber design (particularly the orientation of the heat transfer surfaces) and the burner aerodynamics affect the peak temperature achieved in the combustion zone and the mixing rate of oxygen with the LPG. Modifications to the burner hardware or to the operating procedures can dramatically reduce NO<sub>x</sub> via changes to peak temperature or mixing. Low excess air (LEA) firing, flue gas recirculation (FGR), staged combustion (SC), or some combination thereof may result in NO<sub>x</sub> reductions of 15 to 75 percent. Also, load reduction usually decreases NO<sub>x</sub> production by decreasing the volumetric heat release in the combustion chamber, thus reducing peak temperatures.

### 2.3.2 Carbon Monoxide Emissions

The rate of CO emissions from gas-fired combustion equipment depends on the efficiency of the final burnout of this last remaining product of incomplete combustion. Carbon monoxide burnout is strongly kinetically controlled. If final burnout is not achieved quickly at high temperatures, a long residence time in the post-furnace zone is required to reduce CO to low levels. Carbon monoxide emissions are thus very sensitive to combustion chamber and burner design and operation. If a unit is operated improperly or not maintained, the resulting emissions of CO (as well as organic compounds) may increase by an order of magnitude. Small boilers, heaters, and furnaces tend to emit more of these pollutants than larger combustors. This is because small units usually have a higher ratio of heat transfer surface area to flame volume leading to reduced flame temperature and combustion intensity and, therefore, lower combustion efficiency than large combustors. Also, these smaller units are usually not well maintained, resulting in operation at either too lean or too rich fuel/air ratios, thus increasing CO.

The presence of CO in the exhaust gases of combustion systems results principally from incomplete fuel combustion. Several conditions can lead to incomplete combustion. These include:

- ! Insufficient oxygen availability;
- ! Extremely high levels of excess air leading to quenching (more common with industrial boilers);
- ! Poor fuel/air mixing;
- ! Cold wall flame quenching;
- ! Reduced combustion temperature;
- ! Decreased combustion gas residence time; and
- ! Load reduction (i.e., reduced combustion intensity).

Since various combustion modifications for NO<sub>x</sub> reduction can produce one or more of the above conditions, the possibility of increased CO emissions is a concern for environmental, energy efficiency, and operational reasons.

#### 2.3.3 Sulfur Oxide Emissions

Sulfur oxides result from oxidation of residual sulfur compounds in the LPG either to sulfur dioxide (SO<sub>2</sub>) or sulfur trioxide (SO<sub>3</sub>). With gaseous fuels, essentially all sulfur is oxidized and emitted with the flue gas. Generally, over 90 percent of SO<sub>x</sub> is in the form of SO<sub>2</sub>. The sulfur content of LPG is very low but will vary with supplier depending on processing prior to distribution.

#### 2.3.4 Particulate Matter Emissions

Particulate matter emissions from LPG combustion are very low and result from soot, aerosols formed by condensible emitted species, or boiler scale dislodged during combustion. Combustible emissions are controllable, in part, by modifications to the combustion conditions. Measurements of condensible emissions are influenced by sampling conditions which affect whether a species is quantified as vapor or particulate.

#### 2.3.5 Organic Compound Emissions

Total organic compounds include volatile organic compounds (VOCs) which remain in a gaseous state in ambient air, semi-volatile organic compounds and condensible organic compounds. According to the Federal Register definition (57 FR 3945), VOC has been defined as any organic compound excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate which participates in atmospheric photochemical reactions. The following additional compounds have been deemed to be of "negligible photochemical reactivity" and also are exempt from the definition of VOC: methane, ethane, methyl chloroform, methylene chloride, and most chlorinated-fluorinated compounds (commonly referred to as CFCs). Although these compounds are considered "exempt" from most ozone control programs due to their low photochemical reactivity rates, they are of concern when developing complete emission inventories which are necessary for the design of effective ozone control strategies. The term TOC will be considered to include all organic compounds, i.e., VOCs plus the "exempt" compounds including methane and ethane, toxic compounds, aldehydes, perchloroethylene, semi-volatiles, and condensibles (as measured by EPA Reference Methods).

Emissions of VOCs are primarily characterized by the criteria pollutant class of unburned vapor phase hydrocarbons. Unburned hydrocarbon emissions can include essentially all vapor phase organic compounds emitted from a combustion source. These are primarily emissions of aliphatic, oxygenated, and low molecular weight aromatic compounds which exist in the vapor phase at flue gas temperatures. These emissions include all alkanes, alkenes, aldehydes, carboxylic acids, and substituted benzenes (e.g., benzene, toluene, xylene, ethyl benzene, etc.).

The remaining organic emissions are composed largely of compounds emitted from combustion sources in a condensed phase. These compounds can almost exclusively be classed into a group known as polycyclic organic matter (POM), and a subset of compounds called polynuclear aromatic hydrocarbons (PNA or PAH). There are also the PAH-nitrogen analogs. Information available in the literature on POM compounds generally pertains to these PAH groups. Polycyclic organic matter emissions are generally less prevalent from LPG and other gaseous fuel combustion than volatile organic emissions because of the fuel structure.

Formaldehyde is formed and emitted during combustion of hydrocarbon-based fuels. Formaldehyde is present in the vapor phase of the flue gas. Since formaldehyde is subject to oxidation and decomposition at the high temperatures encountered during combustion, large units with efficient combustion (resulting from closely regulated air-fuel ratios, uniformly high combustion chamber temperatures, and relatively long retention times) should have lower formaldehyde emission rates than do small, less efficient combustion units.

### 2.3.6 Trace Element Emissions

Trace elements are an important class of air toxics compounds. Their concentration in the flue gas emissions is, however, dominated by the concentration of contaminants in the fuel unless another source such as process material contains trace elements. There is a very low concentration of trace elements in LPG due to its origin (i.e., natural gas wells) or to processing within a refinery. Accordingly, trace element emissions for LPG are very low compared to oil or coal combustion.

### 2.3.7 Carbon Dioxide Emissions

Carbon dioxide is the final product of all hydrocarbon combustion. With LPG combustion, nearly all carbon in the fuel is emitted as CO<sub>2</sub>. Minor amounts, typically 0.01 percent, are emitted as CO, giving a carbon conversion efficiency to the stack of 99.99 percent. Therefore, emission factors for CO<sub>2</sub> can be better approximated using a carbon mass balance than by measurement.

### 2.3.8 Nitrous Oxide Emissions

Nitrous oxide is relatively harmless to human health but is included among greenhouse gases. Numerous measurements made prior to 1988 suggested that N<sub>2</sub>O emissions from gas-fired combustion equipment may be comparable to NO<sub>x</sub> emissions. In 1988, the earlier sampling protocols proved to be faulty resulting in N<sub>2</sub>O generation in the post-test sample processing. Recent N<sub>2</sub>O emissions data indicate that direct N<sub>2</sub>O emissions from conventional gas-fired combustion units are an order of magnitude or more below the measurements made prior to 1988. However, the N<sub>2</sub>O formation and reaction mechanisms are still not well understood or well characterized. Emissions can vary widely from unit to unit, or even for different operating conditions at the same unit. Additional sampling and research is needed to fully characterize N<sub>2</sub>O emissions and to

understand the N<sub>2</sub>O formation mechanism. It has been shown in some cases that N<sub>2</sub>O increases with decreasing combustion temperature, so some lower-temperature LPG-fired domestic heating equipment may be suspect.

#### 2.3.9 Fugitive Emissions

Fugitive emissions are unducted pollutants escaping an industrial process via leakage, materials handling, inadequate operational control, transfer, storage or distribution. With adequately maintained LPG equipment, fugitive emissions are primarily confined to tank loading transfer operations, and these emissions are controllable. With inadequately maintained equipment, leaks in the distribution system can occur at valves and flanges.

### 2.4 CONTROL TECHNOLOGIES

The pollutant specie of most concern for stationary LPG combustion is NO<sub>x</sub>. Nitrogen oxides are the only pollutants for which controls have been developed for LPG firing in internal combustion sources. Volatile organic compound controls on standby generator engines fueled with LPG are discussed in AP-42 Section 3.4.

The NO<sub>x</sub> control techniques for LPG have generally been adapted from the experience with low NO<sub>x</sub> natural gas firing. However, LPG presents two challenges in translating natural gas technology, however. First, the NO<sub>x</sub>-forming potential with LPG is higher, so that baseline emissions are typically considerably higher for LPG than for natural gas. This is due primarily to the higher heating values and, hence, higher combustion intensity of LPG relative to natural gas. As a result, higher percent reductions may be needed with LPG to comply with an emission standard. In this respect, the NO<sub>x</sub>-forming characteristics of LPG are more similar to light oil. Second, LPG burners are more susceptible to sooting and smoking behavior when modified to off-optimum operation. Thus, attempts to control LPG NO<sub>x</sub> by combustion modification may encounter operational constraints well before the full potential for NO<sub>x</sub> reduction is reached.

Until recently, there has been little regulatory incentive to develop or implement low NO<sub>x</sub> LPG combustion systems. Accordingly, there has been little developmental activity reported. Flue gas recirculation, a traditional technique with natural gas, has been attempted on a small commercial boiler fired with LPG<sup>2</sup>. NO<sub>x</sub> emissions from

propane combustion were reduced by approximately 50 percent by recirculating 16 percent of the flue gas<sup>2</sup>. For a pilot scale unit, NO<sub>x</sub> emissions from butane combustion were reduced by approximately 79 percent by recirculating approximately 30 percent of the flue gas<sup>3</sup>.

Recent SCAQMD regulations have prompted development of advanced low NO<sub>x</sub> techniques for firetube and watertube boilers. The SCAQMD Rule 1146 for existing boilers and stringent new source review limits for new boilers have created the need for controlled NO<sub>x</sub> emissions of 30 to 40 ppm. Numerous boiler operators are planning to use propane or butane to replace distillate oil as an adjunct or backup to natural gas pursuant to the fuel oil phaseout. Accordingly, several boiler or burner vendors have started to develop low NO<sub>x</sub> burners for LPG to comply with Rule 1146. One manufacturer of low NO<sub>x</sub> burners reported a 65 percent reduction of NO<sub>x</sub> emissions using a low NO<sub>x</sub> burner and water injection on a propane-fired boiler located in the SCAQMD<sup>4</sup>. The boiler was firing propane as a backup fuel to natural gas. There are several propane-fired installations in the SCAQMD required to meet a NO<sub>x</sub> limit of 40 ppm at 3 percent O<sub>2</sub>. Water or steam injection is used as a trimming technique if compliance cannot be reached by low-NO<sub>x</sub> burners (LNB) alone. The water is injected into the primary flame zone usually through the oil guns. Most vendors are now prepared to warrant 30 or 40 ppm NO<sub>x</sub> emissions (referenced to 3 percent oxygen) for existing or new boilers.

TABLE 2-1. COMPARISON OF LPG AND NATURAL GAS SALES FOR 1989<sup>1</sup>

	Annual sales, billion KW-hr (trillion Btu)		
	Residential	Commercial	Industrial
LPG	150 (505)	26 (89)	480 (1627)
Natural Gas	1310 (4471)	643 (2193)	885 (3010)

## REFERENCES FOR SECTION 2

1. Gas Facts: 1990 Data, The American Gas Association, Arlington Va. 1991.
2. Nitrous Oxide Reduction with the Weishaupt Flue Gas Recirculation System, Weishaupt Research and Development Institute, Jan. 1987.
3. Some Examples of Combustion Tests for Putting New Fuels to Practical Use, Ikebe et al, IHI Engineering Review, Oct. 1976.
4. Phone communication memorandum dated May 5, 1992. Conversation between B. Lusher of Acurex Environmental, Research Triangle Park, N.C., and G. Constonaine of Hague International.

### 3. GENERAL DATA REVIEW AND ANALYSIS PROCEDURE

This section summarizes the procedures and criteria used for the literature search and data evaluation.

#### 3.1 CRITERIA POLLUTANTS

##### 3.1.1 Literature Search

An extensive literature search was conducted to identify sources of criteria and non-criteria emissions data for LPG combustion. The following sources were searched for emissions data:

##### Literature

- ! Existing AP-42 background files
- ! Files maintained by the EPA's Emission Standards Division and Emission Factor and Methodologies Section
- ! National Technical Information Service (NTIS) documents
- ! EPA contractor files
- ! NO<sub>x</sub>, SO<sub>x</sub>, and PM symposia

##### Personal contacts

- ! Regulatory agencies, primarily the South Coast Air Quality Management District
- ! Southern California Gas Company
- ! Low NO<sub>x</sub> burner (LNB) manufacturers and boiler manufacturers
- ! An LPG supplier who advises customers on conversion issues and regulatory requirements
- ! An LPG systems contractor conducting propane boiler conversions in Southern California

The main conclusion drawn from the literature search was that little has been published regarding emissions from LPG combustion. The SCAQMD is a potential source of future emissions data for LPG since they are the repository of compliance tests for numerous propane and butane conversions completed or planned in the Los Angeles basin. These results were not available within the schedule constraints for this update. Two source reports were requested from SCAQMD for compliance testing conducted on two boilers believed to be burning LPG and propane. These requests were added by SCAQMD to a waiting list. If data are received from SCAQMD or other sources subsequent to the completion of this update, the data will be added to the Background File for this section for consideration during the next update.

Two reports containing LPG emissions data were obtained from the Southern California Gas Company. One report contains emissions data for propane and natural gas in three different boilers equipped with flue gas recirculation, including one set of baseline concentrations for natural gas and propane fired in the same boiler.<sup>1</sup> The second source is an article which presents emissions data for natural gas, propane and butane firing in a pilot-scale boiler equipped with flue gas recirculation<sup>2</sup>. Emissions rates are given as a function of flue gas recirculation rates which varied from 0 to 40 percent.

One LNB manufacturer provided emission measurements for a propane-fired boiler<sup>3</sup>. The boiler was equipped with a LNB and water injection. At full load the NO<sub>x</sub> concentration was 52 ppm; with water injection the NO<sub>x</sub> concentration decreased to 17.9 ppm. This reduction meets the SCAQMD Rule 1146 standard of 40 ppm NO<sub>x</sub> at 3 percent O<sub>2</sub>.

Another LNB manufacturer provided some emissions data for a propane-fired industrial packaged watertube boiler. However, the process was not identified in the information provided. Moreover, the NO<sub>x</sub> emissions were extremely high (279 ppm at 4 percent O<sub>2</sub>) when compared to the other data obtained. As a result, these data were excluded from further consideration.

### 3.1.2 Literature Evaluation

The data obtained from the literature search were reviewed to determine their suitability for use in emission factor calculations. Checklists were employed to standardize and document this evaluation. The completed checklists were placed in the background file for this update to AP-42. Data with the following characteristics were excluded from further consideration:

1. Test series averages reported in units that cannot be converted to the selected reporting units;
2. Test series representing incompatible test methods (i.e., comparison of EPA Method 5 front-half with EPA Method 5 front- and back-half);
3. Test series of controlled emissions for which the control device is not specified;
4. The series in which the boiler design and operating conditions are not clearly identified and described; and
5. Test series in which it is not clear whether the emissions were baseline or controlled.

Data sets that were not excluded were assigned a quality rating. The rating system used was that specified in the draft EPA document, "Technical Procedures For Developing AP-42 Emission Factors And Preparing AP-42 Sections" (March 6, 1992).

The data were rated as follows:

- A: Multiple tests performed on the same source using sound methodology and reported in enough detail for adequate validation. These test are not necessarily EPA reference method tests, although such reference methods are preferred and certainly to be used as a guide.
- B: Tests that were performed by a generally sound methodology but lack enough detail for adequate validation.
- C: Tests that were based on an untested or new methodology or that lacked a significant amount of background data.
- D: Tests that were based on a generally unacceptable method but may provide an order-of-magnitude value for the source.

The following criteria were used to evaluate source test reports for sound methodology and adequate detail:

1. Source operation. The manner in which the source was operated is well documented in the report. The source was operating within typical parameters during the test.
2. Sampling procedures. The sampling procedures conformed to generally acceptable methodology. If actual procedures deviated from accepted methods, the deviations are well documented. When this occurred, an evaluation was made of the extent such alternative procedures could influence the test results.
3. Sampling and process data. Adequate sampling and process data are documented in the report. Many variations can occur unnoticed and without warning during testing. Such variations can induce wide deviations in sampling results. If a large spread between test results cannot be explained by information contained in the test report, the data are suspect and were given a lower rating.
4. Analysis and calculations. The test reports contain original raw data sheets. The nomenclature and equations used were compared to those (if any) specified by EPA to establish equivalency. The depth of review of the calculations was dictated by the reviewer's confidence in the ability and conscientiousness of the tester, which in turn was based on factors such as consistency of results and completeness of other areas of the test report.

### 3.2 NONCRITERIA POLLUTANTS

This update was done in parallel with updates to other sections of AP-42 Chapter 1. As part of these other updates, extensive literature searches were made of the likely sources of test data on non-criteria pollutant species, e.g. speciated VOC, air toxics, and N<sub>2</sub>O. Sources searched included EPA emissions data bases and research project reports, symposia and journals, industry trade associations, and computerized literature data bases. No noncriteria pollutant data directly related to LPG combustion were identified during the search. Accordingly, no emission factor development was possible for noncriteria species. In the absence of test data, order of magnitude qualitative estimates of LPG emissions may be made using natural gas or distillate oil test results for comparable equipment designs.

### 3.3 FUGITIVE EMISSIONS

Fugitive emissions have not historically been covered in Chapter 1 of AP-42. Chapter 4 contains emission factors for evaporative losses from petroleum storage facilities and will continue to be the source of such data.

A literature search was conducted to quantify fugitive emissions from leaking seals and fittings that would be present in the fuel feed system for LPG combustion sources. These fugitive sources include valves, flanges, relief valves and open-end lines. The literature evaluation verified the conclusions of previous attempts at determining emission factors for VOCs in the Synthetic Organic Chemical Manufacturing Industry (SOCMI). During the establishment of proposed standards for fugitive VOC emissions from the SOCMI, EPA determined (1) that the only quality emission factor data were generated during an EPA study of 13 petroleum refineries and (2) that the highest quality data for leakages from each equipment type resulted from an EPA study of leak frequency in the SOCMI. Data from these two EPA references were subjectively rated B quality per the general guidelines previously described. Because of the lack of sufficient data for calculating new emission factors for fugitive emissions, the remainder of the references obtained were not used and, therefore, not rated.

## REFERENCES FOR CHAPTER 3

1. Nitrous Oxide Reduction with the Weishaupt Flue Gas Recirculation System, Weishaupt Research and Development Institute, Jan. 1987.
2. Some Examples of Combustion Tests for Putting New Fuels to Practical Use, Ikebe et al, IHI Engineering Review, Oct. 1976.
3. Phone communication memorandum dated May 5, 1992. Conversation between B. Lusher of Acurex Environmental and G. Constonaine of Hague International.
4. Phone communication memorandum dated May 5, 1992. Phone conversation between B. Lusher of Acurex Environmental and S. Londerville of The Coen Company.

## 4. EMISSION FACTOR DEVELOPMENT

In each AP-42 section, tables of emission factors are presented for pollutants associated with equipment operations within the subject source category. The reliability or quality of each of these emission factors is indicated in the tables by an overall Emission Factor Quality Rating ranging from A (excellent) to E (poor). These ratings incorporate the results of the quality and quantity evaluations on the data sets used to calculate the final emission factors, as described in Chapter 3. The overall emission factor quality ratings are described as follows:

A--Excellent: Developed only from A-rated test data taken from many randomly chosen facilities in the industry population. The source category is specific enough so that variability within the source category population may be minimized.

B--Above average: Developed only from A-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industries. As in the A-rating, the source category is specific enough so that variability within the source category population may be minimized.

C--Average: Developed only from A- and B-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry.. As in the A-rating, the source category is specific enough so that variability within the source category population may be minimized.

D--Below average: The emission factor was developed only from A- and B-rated test data from a small number of facilities, and there is reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of the emission factor are noted in the emissions factor table.

E--Poor: The emission factor was developed from C- and D-rated test data, and there is reason to suspect that the facilities tested do not represent a random

sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of these factors are always noted.

The use of these criteria is somewhat subjective and depends to an extent on the individual reviewer. Details of the rating of each candidate emission factor are provided in the following paragraphs.

#### 4.1 CRITERIA POLLUTANTS

##### 4.1.1 Review of Previous Data

Previously, criteria pollutant emission factors were assumed to be equivalent to the natural gas emission factors on a lb/MMBtu (or kg/MW) basis, except for the SO<sub>x</sub> emission factor which was based on fuel sulfur content. There was little quantitative basis for this assumption, however.

Using the new AP-42 evaluation criteria, the prior criteria pollutant emission factors were designated as E quality because these factors were developed from essentially no LPG data and from an erroneous assumption about comparability to natural gas. Although the SO<sub>x</sub> emission factor is based on fuel sulfur content, the relative amounts of SO<sub>2</sub> and SO<sub>3</sub> (which make up the SO<sub>x</sub>) are not based on LPG data but rather the assumption that all input fuel sulfur is emitted as SO<sub>2</sub>. For this reason, the emission factor for SO<sub>2</sub> was designated as E quality.

##### 4.1.2 Review of New Data

The Weishaupt report contains one baseline NO<sub>x</sub> test for natural gas, and propane fired in a 8 MW (23 MMBtu/hr) boiler at full load.<sup>1</sup> For this test, the ratio of propane NO<sub>x</sub> emissions to natural gas NO<sub>x</sub> emissions was 1.6. An emission factor of 1.3 kg NO<sub>x</sub>/thousand liters (11.4 lb NO<sub>x</sub>/thousand gallons) was calculated for the full load concentration of NO<sub>x</sub> from propane combustion using the F-factor from 40 CFR Reference Method 19. This value is lower than the NO<sub>x</sub> emission factor of 1.5 kg NO<sub>x</sub>/thousand liters (12.4 lb NO<sub>x</sub>/thousand gallons) contained in the 1982 version of Section 1.5.

An article from IHI Engineering Review presents NO<sub>x</sub> concentrations from a pilot scale test furnace for methane, propane, and butane.<sup>2</sup> These concentrations indicate (1) that NO<sub>x</sub> emissions from propane combustion are 1.3 times greater than those for natural gas and (2) that NO<sub>x</sub> emissions from butane combustion are 1.5 times greater

than those for natural gas. Using the calculation procedure from 40 CFR Appendix A Reference Method 19, the propane emission factor is 1.7 kg NO<sub>x</sub>/thousand liters (14.6 lb NO<sub>x</sub>/thousand gallons) and the butane emission factor is 2.2 kg NO<sub>x</sub>/thousand liters (19.0 lb NO<sub>x</sub>/thousand gallons). The emission factors from the 1982 version of Section 1.5 are 1.5 kg NO<sub>x</sub>/thousand liters (12.4 lb NO<sub>x</sub>/thousand gallons) for propane and 1.6 kg NO<sub>x</sub>/thousand liters (13.2 lb NO<sub>x</sub>/thousand gallons) for butane.

Data from both sources indicate that NO<sub>x</sub> emissions from propane and butane combustion are significantly higher than the NO<sub>x</sub> emissions generated from natural gas. The data presented in both of these sources do not specify any protocol for the NO<sub>x</sub> emissions data collection. It is assumed that the data were collected using continuous emission monitoring equipment. No information is presented on the amount of testing conducted to generate the results. Therefore, both of these data sources were assigned a C data quality ranking. These sources are useful for comparing propane and butane emissions to natural gas emissions.

The SO<sub>x</sub> emission factor was recalculated using the exact procedure that was used to generate the previous emission factor in 1982. The ratio of m<sup>3</sup> gas/thousand liters liquid was changed based on information in Reference 3. The calculated propane SO<sub>x</sub> emission factor (in kg SO<sub>2</sub>/1,000 liters) is 0.012 S, where S is fuel sulfur content expressed as gr sulfur/100 ft<sup>3</sup> gas vapor; the butane emission factor (in kg SO<sub>2</sub>/1,000 liters) is 0.011 S. For example, if the butane sulfur content is 0.18 gr/100 ft<sup>3</sup>, the emission factor would be (0.011 x 0.18 =) 0.0020 kg SO<sub>2</sub>/1,000 liters of butane burned. Sample calculations for the SO<sub>2</sub> emission factor and other unit conversions are contained in Appendix A.

The SO<sub>2</sub> emission factors have been assigned a rating of E because the emission factors are based on feed gas sulfur content and actual SO<sub>2</sub> emissions were not measured. These emission factors are conservative and assume all of the input sulfur is emitted as SO<sub>2</sub>.

#### 4.1.3 Compilation of Emission Factors

The development approach for new SO<sub>2</sub> emission factors is discussed above. Due to the lack of LPG combustion emissions data, emission factors for other criteria pollutants in this version were based on the natural gas combustion criteria emission

factors. The natural gas emission factors were converted to LPG factors on a heating value basis using the following heating values: 9,340 kcal/m<sup>3</sup> (1050 Btu/ft<sup>3</sup>) for natural gas; 6,090 kcal/liter (91,500 Btu/gal) for propane; and 6,830 kcal/liter (102,600 Btu/gal) for butane<sup>3</sup>. The NO<sub>x</sub> emission factors calculated from the natural gas emission factors for propane and butane were multiplied by the average ratio of propane and butane emissions to natural gas emissions. The average ratio of NO<sub>x</sub> emissions from propane and butane to natural gas is 1.5. This ratio is based on a limited amount of data, but does provide an order of magnitude estimate of the NO<sub>x</sub> emissions from propane and butane. The TOC emission factor was calculated by adding the methane and non-methane VOC emission factor. The base natural gas emission factors and the corresponding propane and butane emission factors are summarized in Tables 4-1 and 4-2.

#### 4.2 NONCRITERIA POLLUTANTS

No data were available for emissions from LPG combustion for VOC speciation, air toxics, and N<sub>2</sub>O. In the absence of any data, no emission factors can credibly be developed. The natural gas and distillate oil emission factors in AP-42 Sections 1-3 and 1-4 can be consulted for order of magnitude values, but there is no defensible basis to assume the emission factors would be the same for LPG or any other conventional fuel.

For the CO<sub>2</sub> emission factor, the assumption was made that all carbon in the fuel is oxidized to CO<sub>2</sub> and emitted from the stack. Based on this assumption, the emission factors are:

- For propane: 1,500 kg CO<sub>2</sub>/1,000 (12,500 lb CO<sub>2</sub>/1,000 gal), and
- For butane: 1,760 kg CO<sub>2</sub>/1,000 (14,700 lb CO<sub>2</sub>/1,000 gal).

#### 4.3 FUGITIVE EMISSIONS

Fugitive emissions were not considered for emission factor development in the previous version of Section 1.5. Chapter 4 of AP-42 contains emission factors for fugitive releases for most of the activities associated with LPG storage, distribution and transfer. Additional data compilation was attempted for fugitive releases during distribution which were not fully treated in Chapter 4. A total of 10 references were documented and reviewed during the literature search. This group of 10 documents

was reduced to one primary reference using the criteria outlined in Chapter 3. The nine rejected reference documents were not used because of inadequate documentation of operational conditions which could be generalized to emission factor development, or lack of relevance to LPG.

Emission factors for LPG handling and storage are found in Chapter 4 of AP-42. The VOC emission factors for the fuel feed system selected for inclusion in AP-42 were taken directly from the Petroleum Refineries study and the 24-unit SOCFI study included in Reference 4. The factors specified for LPG-fired boilers are the EPA-approved values for valves, flanges, relief valves and open-ended lines handling gases. The data used in calculating these values varied widely for different fluids but the emission factors were derived through a well-described approach developed for the SOCFI fugitive emissions standards proposed by EPA in January, 1981. The procedure used estimates of leaking and non-leaking source emission factors from the refinery data set and applied these factors to the leak frequencies found in the SOCFI 24-unit screening study to yield emission factors for average SOCFI units. The resultant "average" SOCFI factors were considered valid for this update. Table 4-3 presents the proposed VOC emission factors for LPG feed systems.

TABLE 4-1. NATURAL GAS COMBUSTION EMISSION FACTORS

Pollutant	Emission factors, kg/10 <sup>6</sup> m <sup>3</sup> (lb/10 <sup>6</sup> ft <sup>3</sup> )	
	Small industrial boilers <sup>a</sup>	Commercial boilers <sup>b</sup>
Filterable Particulate Matter	100 (6.2)	73 (4.5)
NO <sub>x</sub>	2,258 (140)	1600 (100)
CO	565 (35)	339 (21)
TOC	94 (5.8)	94 (5.8)
SO <sub>2</sub>	9.7 (0.6)	--

<sup>a</sup> Heat input of 10 - 100 MMBtu/hr.

<sup>b</sup> Heat input of 0.3 - <10 MMBtu/hr.

TABLE 4-2. LPG COMBUSTION EMISSION FACTORS

Pollutant	Butane emissions, kg/1000 l (lb/1000 gal)		Propane emissions, kg/1000 l (lb/1000 gal)	
	Industrial boilers	Commercial boilers	Industrial boilers	Commercial boilers
Filterable PM	0.07 (0.6)	0.06 (0.5)	0.07 (0.6)	0.05 (0.4)
NO <sub>x</sub>	2.5 (21)	1.8 (15)	2.3 (19)	1.7 (14)
CO	0.42 (3.6)	0.25 (2.1)	0.38 (3.2)	0.22 (1.9)
CO <sub>2</sub>	1,760 (14,700)	1,760 (14,700)	1,500 (12,500)	1,500 (12,500)
TOC	0.07 (0.6)	0.07 (0.6)	0.06 (0.5)	0.06 (0.5)

<sup>a</sup> All of the criteria pollutants were given an emission factor rating of E. All E-rated emission factors are based on C and D quality data from a small number of facilities not necessarily representative of the industry.

TABLE 4-3. FUGITIVE EMISSION FACTORS FOR VARIOUS EQUIPMENT TYPES<sup>4</sup>

Equipment type	Emission factor,		Factor rating
	kg/hr/source	lb/hr/source	
Valve	0.0056	0.00254	D
Relief valve	0.1040	0.0417	D
Open-ended line	0.0017	0.000771	D
Flange	0.00083	0.000376	D

## REFERENCES FOR CHAPTER 4

1. Nitrous Oxide Reduction with the Weishaupt Flue Gas Recirculation System, Weishaupt Research and Development Institute, Jan. 1987.
2. Some Examples of Combustion Tests for Putting New Fuels to Practical Use, Ikebe et al, IHI Engineering Review, Oct. 1976.
3. Perry's Chemical Engineers' Handbook (Sixth Edition), Robert H. Perry and Don W. Green (Editors), McGraw-Hill Book Company, New York, New York, 1984.
4. Fugitive Emission Sources of Organic Compounds - Additional Information on Emissions, Emission Reductions, and Costs, EPA-450/3-82-010, U.S. Environmental Protection Agency, RTP, NC, April 1982.

## 5. AP-42 SECTION 1.5: LIQUEFIED PETROLEUM GAS COMBUSTION

The revision to Section 1.5 of AP-42 is presented in the following pages as it would appear in the document. A marked-up copy of the 1982 version of this section is included in Appendix B.

APPENDIX A  
SAMPLE CALCULATIONS

SO<sub>x</sub> Emission Factor Calculation

$$(S \text{ grains}/100 \text{ ft}^3)(\text{lb}/7000 \text{ grains})(\text{ft}^3/10^3 \text{ gal})(2 \text{ lb SO}_2/\text{lb S}) = S \text{ lb SO}_2/10^3 \text{ gal}$$

From 40 CFR Appendix A. Reference Method 19.

ppm to lb/10<sup>6</sup> Btu:

ppm NO<sub>x</sub> @ 3% O<sub>2</sub>

$$\text{ppm NO}_x \times (1.194 \times 10^{-1} \text{ lb/scf/ppm NO}_x) = \text{lb/scf}$$

$$E = \text{lb/scf} (8710 \text{ scf}/10^6 \text{ Btu})(20.9/(20.9-3\% \text{ O}_2)) = \text{lb}/10^6 \text{ Btu}$$

lb/10<sup>6</sup> Btu to lb/10<sup>3</sup> gal:

91,500 Btu/gal Propane

102,600 Btu/gal Butane

1050 Btu/ft<sup>3</sup> Natural Gas

$$\text{lb pollutant}/10^3 \text{ gal} = \text{lb pollutant}/10^6 \text{ ft}^3 \text{ natural gas} \times 1050 \text{ Btu}/\text{ft}^3 \times 0.915 \times 10^8 \text{ Btu}/10^3 \text{ gal}$$

$$\text{lb pollutant}/10^3 \text{ gal} = \text{lb pollutant}/10^6 \text{ ft}^3 \text{ natural gas} \times 1050 \text{ Btu}/\text{ft}^3 \times 1.026 \times 10^8 \text{ Btu}/10^3 \text{ gal}$$

APPENDIX B  
MARKED-UP 1982 SECTION 1.5

REPORT ON REVISIONS TO  
5TH EDITION AP-42  
Section 1.5  
Liquefied Petroleum Gas Combustion

Prepared for:

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B-xxxvi

## Table of Contents

	Page
1.0 INTRODUCTION .....	1-1
2.0 REVISIONS .....	2-1
2.1 General Text Changes .....	2-1
2.2 Greenhouse Gases .....	2-1
2.2.1 Carbon Dioxide, CO <sub>2</sub> .....	2-1
2.2.2 Methane, CH <sub>4</sub> .....	2-2
2.2.3 Nitrous Oxide, N <sub>2</sub> O .....	2-2
3.0 REFERENCES .....	3-1
4.0 REVISED SECTION 1.5 .....	4-1
5.0 EMISSION FACTOR DOCUMENTATION, APRIL 1993 .....	5-1

## 1.0 INTRODUCTION

This report supplements the Emission Factor (EMF) Documentation for AP-42 Section 1.5, Liquified Petroleum Gas Combustion, dated April 1993. The EMF describes the source and rationale for the material in the most recent updates to the 4th Edition, while this report provides documentation for the updates written in both Supplements A and B to the 5th Edition.

Section 1.5 of AP-42 was reviewed by internal peer reviewers to identify technical inadequacies and areas where state-of-the-art technological advances need to be incorporated. Based on this review, text has been updated or modified to address any technical inadequacies or provide clarification. Additionally, emission factors were checked for accuracy with information in the EMF Document and new emission factors generated if recent test data were available.

If discrepancies were found when checking the factors with the information in the EMF Document, the appropriate reference materials were then checked. In some cases, the factors could not be verified with the information in the EMF Document or from the reference materials, in which case the factors were not changed.

Four sections follow this introduction. Section 2 of this report documents the revisions and the basis for the changes. Section 3 presents the references for the changes documented in this report. Section 4 presents the revised AP-42 Section 1.5, and Section 5 contains the EMF documentation dated April 1993.

## 2.0 REVISIONS

This section documents the revisions made to Section 1.5 of the 5th Edition of AP-42.

### 2.1 General Text Changes

Text was added concerning firing practices based on information in the EMF Document. Also, at the request of EPA, metric units were removed.

### 2.2 Greenhouse Gases

#### 2.2.1 Carbon Dioxide, CO<sub>2</sub>

The CO<sub>2</sub> factors in Table 1.5-1 were recalculated assuming 99.5 percent conversion of fuel carbon to CO<sub>2</sub> instead of the 100 percent used in earlier AP-42 Version 5. Assuming 99.5 percent conversion of fuel carbon content to CO<sub>2</sub> during combustion, the CO<sub>2</sub> emission factors in Table 1 were computed.<sup>1-3</sup>

**Table 1. Default CO<sub>2</sub> Emission Factors for Liquid Fuels  
Quality Rating: B**

Fuel Type	%C <sup>a</sup>	Density <sup>a</sup> (lb/gal)	New Emission Factor (lb/1000 gal) <sup>a</sup>	AP-42 EF (lb/1000 gal)	AP-42 Rating
LPG-Propane	80.7	4.24	12,500	12,500	E
LPG-Butane	80.7	4.84	14,300	14,700	E

<sup>a</sup> Reference 4. "B" factor assigned because of the varying compositions of LPG gas.

<sup>b</sup> References 5-6.

<sup>c</sup> The following equation was used to develop the emission factor equation for LPG:

$$\frac{44 \text{ lb CO}_2}{12 \text{ lb C}} \times 0.995 \times 4.24 \frac{\text{lb}}{\text{gal}} \times \frac{1}{100\%} \times 80.7\% \times 1000 = 12,500 \frac{\text{lb CO}_2}{1000 \text{ gal}}$$

Where: 0.995 = fraction of fuel oxidized during combustion (Reference 1-3);  
 44 = molecular weight of CO<sub>2</sub>;  
 12 = molecular weight of carbon; and  
 4.24 lb/gal = density of LPG-Propane (AP-42 Appendix A).

### 2.2.2 Methane, CH<sub>4</sub>

Table 1.5-2 lists total organic compound (TOC) emission factors but does not contain a factor for CH<sub>4</sub>. One factor for commercial/institutional data was obtained, but source test data was unavailable for verification. This factor was therefore assigned an "E" rating and appears in Table 2:

**Table 2. CH<sub>4</sub> Emission Factors for LPG Combustion<sup>a</sup>  
 (lb CH<sub>4</sub>/1000 gal)**

Combustion Category	EF Rating	EF
Commercial/institutional boilers	E	0.25

<sup>a</sup> Reference 7.

### 2.2.3 Nitrous Oxide, N<sub>2</sub>O

Only one value for N<sub>2</sub>O emissions from LPG combustion (Reference 2) was available. The source data was not listed, so the factor was given an "E" rating.

**Table 3. N<sub>2</sub>O Emission Factors for LPG Combustion<sup>a</sup>**

(lb N<sub>2</sub>O/1000 gal)

<b>Process</b>	<b>EF Rating</b>	<b>EF</b>
Industrial Boilers	E	0.9

<sup>a</sup> Reference 2.

### 3.0 REFERENCES

1. G. Marland and R.M. Rotty, "Carbon Dioxide Emissions from Fossil Fuels: A procedure for Estimation and Results for 1951-1981," DOE/NBB-0036 TR-003, Carbon Dioxide Research Division, Office of Energy Research, U.S. Department of Energy, Oak Ridge, TN, 1983.
2. A. Rosland, *Greenhouse Gas Emissions In Norway: Inventories And Estimation Methods*, Oslo: Ministry of Environment, 1993.
3. *Sector-Specific Issues And Reporting Methodologies Supporting The General Guidelines For The Voluntary Reporting Of Greenhouse Gases Under Section 1605(b) Of The Energy Policy Act Of 1992*, DOE/PO-0028, Volume 2 of 3, U.S. Department of Energy, 1994.
4. K. Dahlberg *et al.*, *Emissions Of  $N_2O$ , CO,  $CO_2$ , COS, and  $CS_2$  From Stationary Combustion Sources*. Institute Vatten-Luftvaardsforsk, Sweden, [Publ.] B, IVL B 891, 1988. 23 pp.
5. R. H. Perry and D. Green, *Perry's Chemical Engineers\* Handbook*, Sixth ed., New York: McGraw Hill, 1984.
6. *Compilation Of Air Pollutant Emission Factors, Volume I: Stationary Point And Area Sources*, U.S. Environmental Protection Agency, AP-42. Fifth Edition. Research Triangle Park, NC, 1995.
7. Ortech Corporation, *Inventory Methods Manual For Estimating Canadian Emissions Of Greenhouse Gases*, Prepared for Environment Canada, 1994.

#### 4.0 REVISED SECTION 1.5

This section contains the revised Section 1.5 of AP-42, 5th Edition. The electronic version can be located on the EPA TTN at <http://www.epa.gov/ttn/chief/ap42c1.html>

## 5.0 EMISSION FACTOR DOCUMENTATION, APRIL 1993

This section contains the Emission Factor Documentation for Section 1.5, dated April 1993. The electronic version can be located on the EPA TTN at <http://www.epa.gov/ttn/chief/ap42c1.html>. The zipped file on the TTN contains this (1996) background report as well as the 1993 Emission Factor Documentation.