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Project Summary

Assessment of Atmospheric Emissions from Petroleum Refining

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This study was conducted to define the atmospheric emissions from petroleum refineries and to assess their impact on the atmosphere. The sources of hydrocarbon and other pollutants were identified. Fugitive hydrocarbon emissions were found to be significant; therefore, a field sampling program was carried out to measure these and other emissions. Sampling programs were conducted at thirteen petroleum refineries throughout the United States. The rates of nonmethane hydrocarbon emissions were determined from valves, flanges, pump seals, compressor seals, pressure relief valves, drains, and cooling towers. Of these sources, valves were found to be the largest emission contributor. Emission rates of hydrocarbons and other pollutants were measured from FCCU regenerator stacks, heater stacks, sulfur recovery unit stacks, and other process sources.

As part of the field sampling program in refineries, the effect of valve maintenance procedures in reducing valve emissions was evaluated. Emission factors for the various fugitive sources were determined; individual organic species in selected refinery streams and emissions were identified; and a model refinery was developed. The results of this field sampling program were used to estimate the losses of hydrocarbon species and other pollutants from the refinery. Atmospheric dispersion modeling was then used to estimate the impact of the model refinery on the surrounding atmosphere.

This publication is a summary of the complete project report entitled "Assessment of Atmospheric Emissions from Petroleum Refining." The complete report can be purchased from the National Technical Information Service. The report was prepared in five volumes:*(See Page 2)*

Introduction

This assessment study of the atmospheric emissions from petroleum refineries was conducted under EPA Contract Numbers 68-02-2665 and 68-02-2147, Exhibit B. The program addressed important environmental questions regarding the effects of refineries on air quality. The three primary objectives of the program were:

1. quantification of fugitive hydrocarbon emissions from petroleum refineries,
2. evaluation of existing and developing refinery control technologies, and
3. assessment of the potential impact of atmospheric refinery emissions on the surrounding environment.

During the three-year study period, the program evolved to focus on these three objectives. The program was originally planned only to address objectives

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2 and 3. Objective 1, however, was added after work was initiated. Several factors contributed to this.

As work began, it became evident that fugitive emissions were a large, if not the largest, source of hydrocarbon emissions from refineries. Moreover, quantitative information concerning fugitive emissions from refineries was scarce. Because of these developments, the program was modified to incorporate objective 1.

This objective was given further emphasis by the Clean Air Act and its emissions off-set regulations. Compliance with these rules necessitated emission factors for use in off-set calculations.

The fugitive hydrocarbon emissions were quantified through field testing at thirteen petroleum refineries located throughout the United States. Refinery process technology was characterized to estimate process and fugitive emissions to the atmosphere from individual types of process units. Data from the field sampling program were used in the evaluation of some existing and developing control technologies. Information was also obtained from vendors, equipment manufacturers, and literature sources.

During the field sampling program, selected refinery streams and atmospheric emissions were analyzed to identify and quantify individual stream components. This knowledge was combined with the emission factors for fugitive and process emissions to develop estimates of the losses of hydrocarbon species and other compounds from a model refinery. Atmospheric dispersion models were used to estimate the concentrations of emitted materials in the surrounding environment.

Conclusions

Fugitive emission sources are categorized as either "baggable" or "nonbaggable" sources. Baggable sources are those that can be enclosed in some type of enclosure or "bag" to measure their emission rates. Baggable source types include valves, open-ended lines, flanges, pump seals, compressor seals, drains, and relief valves.

Nonbaggable sources of fugitive emissions are too large or diffuse to enclose. Emissions estimates must be made by indirect means. Nonbaggable sources include cooling towers, wastewater treating units, spills, turnarounds, blind changing, coking, air blowing, vacuum jets, barometric condensers, and sampling operations. Of the nonbaggable sources, only cooling towers, oil-water separators, and dissolved air flotation (DAF) units were actually sampled in this study. Data from cooling tower sampling were used to develop emission factors; data from oil-water separators and DAF units were inconclusive and emission factors were not developed for these sources.

Five major conclusions may be drawn about fugitive emissions in refineries.

1. Substantial nonmethane hydrocarbon emissions occur from fugitive emission sources in refineries. The estimated nonmethane hydrocarbon emissions from eight sources (valves, flanges, pump seals, compressor seals, drains, pressure relief valves, covered API separators, and cooling towers) in the major process units of a hypothetical 330,000 BPD refinery are 630 pounds per hour (approximately 2,600 tons per year).

2. The only equipment or process variable found to correlate with fugitive emission rates was the volatility and/or the phase of the process stream.

3. Valves were found to be the largest contributors of fugitive emissions from baggable sources types. Valves are responsible for about 50-60 percent of the nonmethane hydrocarbons emitted from baggable sources in the major process units of a hypothetical 330,000 BPD refinery.

4. The major portion of fugitive nonmethane hydrocarbon emissions from any baggable source type comes from a small fraction of the sources. For example, only one percent of valves in gas-vapor service account for 70 percent of the fugitive emissions from this source.

5. It is possible to estimate fugitive hydrocarbon emission rates using portable hydrocarbon detectors as monitoring devices. It was found that the measured hydrocarbon leak rate from baggable sources could be correlated with the hydrocarbon concentration very near the site of the leak. The correlations are useful in estimating the mean leak rate when a large number (> 100) of sources are monitored.

Pollution control technology for refinery emission sources was also reviewed and evaluated during this study. It was determined that effective control methods are available for the majority of hydrocarbon emission sources in refineries. However, these methods, currently used in some refineries, cannot be universally applied. Safety and economic factors may deter their use in some refineries.

Atmospheric modeling of the emissions from a model refinery were carried out as part of an environmental assessment. The dispersion modeling results indicate that hydrocarbon emissions are potentially significant atmospheric pollutants. Ambient levels of particulate matter, sulfur oxides, nitrogen oxides, and carbon monoxide were all predicted to be well below the National Ambient Air Quality Standards (NAAQS). Assessment of the impact of the model refinery on Prevention of Significant Deterioration (PSD) increments, however, was not conducted.

Results

The major results of the fugitive emissions sampling and maintenance evaluation are briefly summarized.

Fugitive Emissions and Emission Factors

The emissions data obtained during the sampling of baggable sources was found to be most conveniently grouped for analyses into twelve categories for presentation of results and emission factor development. These twelve categories are:

1. valves - gas/vapor stream,
2. valves - light liquid/two-phase streams,
3. valves - heavy liquid streams,
4. valves - streams containing > 50% hydrogen,
5. open-ended lines (all streams),
6. pump seals - light liquid streams,
7. pump seals - heavy liquid streams,
8. compressor seals - hydrocarbon streams,
9. compressor seals - streams containing > 50% hydrogen,
10. flanges - all streams,
11. drains - all streams, and
12. relief valves (gas/vapor streams venting directly to atmosphere).

"Gas-vapor" streams consist of those hydrocarbon streams which are in the gas phase at the process conditions. Two-phase streams and hydrocarbon liquids with boiling points below kerosene are included as "light liquid/two-phase" streams. Hydrocarbon streams consisting primarily of kerosene and/or heavier liquids are considered to be in the "heavy liquid" category.

The estimated emission factors for nonmethane hydrocarbon emissions for the seven types of baggable sources are summarized in Table 1. Confidence intervals are given in each case for the estimated emission factor. This confidence interval represents the range of values expected with 95 percent confidence which, includes the average emission rate for all sources of the particular type in all U.S. refineries. The confidence intervals also include consideration of both potential biases and random variation.

Baggable sources in refineries were screened to locate those sources that were emitting hydrocarbons. One of the important results of this study has been the establishment of relationships between baggable source "screening values" and corresponding hydrocarbon leak rate. "Screening values" are the maximum hydrocarbon concentrations detected at the emission source using sensitive hydrocarbon detectors. Nomographs were developed which relate the predicted average leak rate to the screening values for the various source and stream types. The nomograph for valves in gas-vapor service is given in Figure 1. This is presented as an example; nomographs for all source and stream types are presented in the full report (Volume 1).

Table 1. Estimated Vapor Emission Factors for Nonmethane Hydrocarbons from Baggable Sources

Source Category	Emission Factor Estimate		95% Confidence Interval for Emission Factor	
	(lb/hr/source)[a]	(kgk/hr/source)[a]	(lb/hr/source)[b]	(kg/hr/source)[b]
Valves				
Gas-Vapor Streams	0.059	0.0268	(0.030, 0.110)	(0.014, 0.049)
Light Liquid/Two-Phase	0.024	0.0109	(0.017, 0.036)	(0.0077, 0.016)
Heavy Liquid	0.0005	0.00023	(0.0002,0.0015)	(0.0001, 0.00068)
Hydrogen	0.018	0.00816	(0.007, 0.045)	(0.0032, 0.020)
Open-Ended Lines	0.005	0.0023	(0.0016,0.016)	(0.00073,0.0073)
Pump Seals				
Light Liquid Streams	0.25	0.113	(0.16, 0.37)	(0.073, 0.17)
Heavy Liquid Streams	0.046	0.0209	(0.019, 0.11)	(0.0086, 0.050)
Drains	0.070	0.0318	(0.023, 0.20)	(0.010, 0.091)
Flanges	0.00056	0.00025	(0.0002,0.0025)	(0.0001, 0.0011)
Relief Valves (Gas/Vapor Streams)	0.19	0.0862	(0.070, 0.49)	(0.032, 0.22)
Compressor Seals				
Hydrocarbon Service	1.4	0.635	(0.66, 2.9)	(0.30, 1.3)
Hydrogen Service	0.11	0.0499	(0.05, 0.23)	(0.02, 0.10)

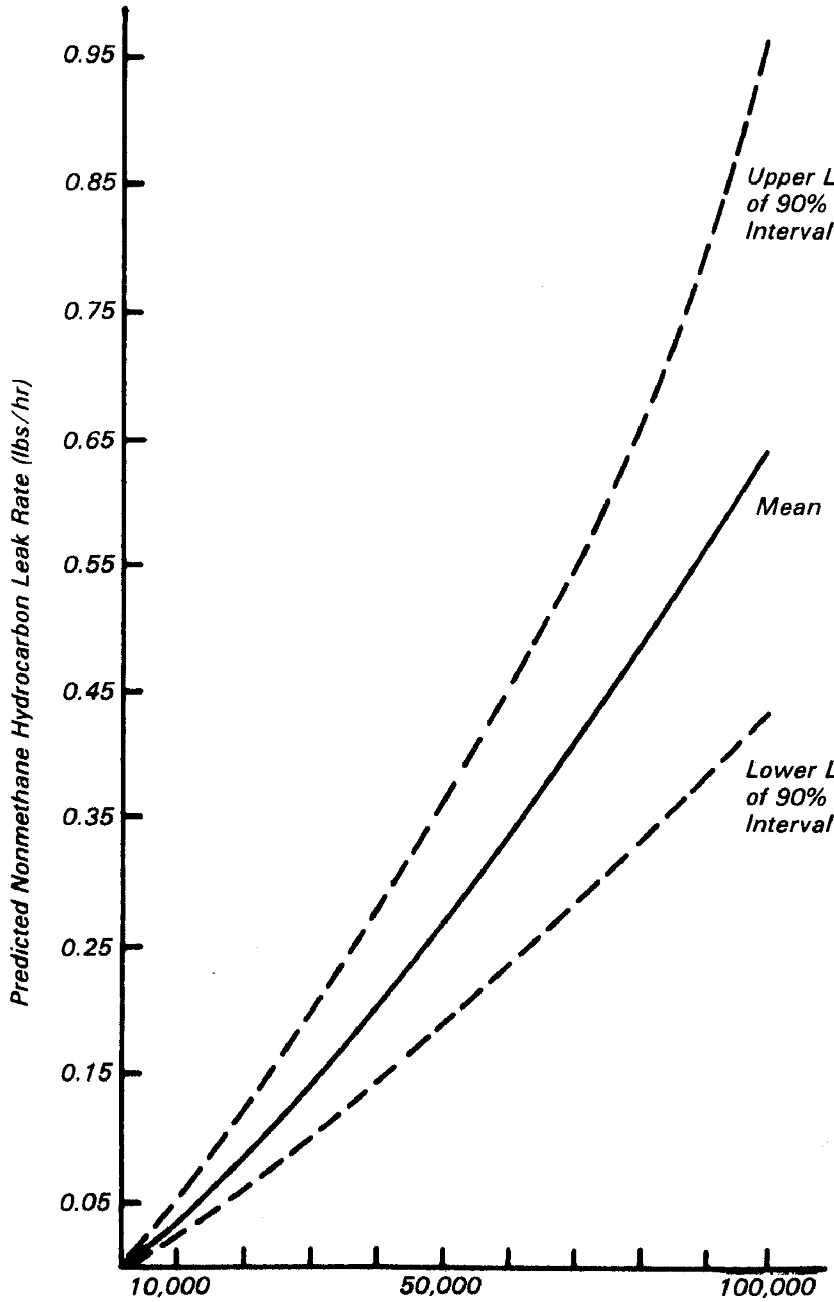
[a]The estimated mean level of emissions from all sources of this type in U.S. refineries. This factor is an average and incorporates the fact that a significant number of sources have no emissions while others have emissions ranging from 10^{-5} to 10 lbs/hr.
[b]The statistical procedures used to construct these intervals account for both systematic and random errors in experimental design, sampling, chemical analysis, and statistical analysis. The procedures used are such that at least 95% of the intervals will include the mean emission factor for a particular source category.

Maintenance Evaluation

A study to determine the short-term effect of maintenance on valve emissions was conducted. Two types of maintenance were studied. Directed maintenance which involves simultaneous maintenance and monitoring until no further reduction in hydrocarbon detector readings can be achieved, and undirected maintenance, which is not monitored.

The study indicated that directed maintenance can produce greater reductions in emissions than undirected maintenance. It also showed that the percentage emission reduction is lower for valves with initially smaller leak rates. Undirected maintenance actually increased average emissions from valves with initial leak rates ≤ 0.001 pounds per hour.

The results of the study are presented in Table 2. Three measures of the effectiveness of maintenance are presented: average percent reduction, weight percent reduction, and median percent reduction. The average percent reduction indicates the average effectiveness of maintenance on the individual valves in each screening value range. The weight percent reduction is a measure of the total reduction in the mass of emissions for all valves in each screening value range. The median percent reduction is the middle percent reduction in emissions after all the individual percent reductions in each category



Maximum Screening Value (ppmv) at the Source Using J. W. Bacharach TLV Sniffer Calibrated with Hexane.*

**A portable hydrocarbon detector equipped with a catalytic element as a detector.*

Figure 1. *Nomograph for predicting total nonmethane hydrocarbon leak rates from maximum screening values—valves, gas/vapor streams.*

have been arranged in order of magnitude.

Both the average percent reduction and the weight percent reduction are highly influenced by extremes within the leak rate range. The median percent reduction is a more robust measure of central tendency. It cannot be affected by the very large negative values of percent reduction encountered at low leak rates (particularly with undirected maintenance).

As indicated in Table 2, only a relatively small number of valves were evaluated. Thus, the absolute values of the emission reductions presented should be used with caution.

Table 2. *Summary of Valve Maintenance Data*

Screening Value Range, ppmv	Undirected Maintenance: Number of Valves	Undirected Maintenance: Percent Emission Reduction	Directed Maintenance: Number of Valves	Directed Maintenance: Percent Emission Reduction
<5,000	28	P_a = -312 (-950,100)[a]	11	P_a = 54 (4,100)
		P_w = 33 (-39,100)		P_w = 86 (72,99)
		P_m = 29 (-1,79)		P_m = 88 (18,98)
5,000-50,000	15	P_a = 37 (-28,100)	8	P_a = 82 (65,98)
		P_w = 67 (34,100)		P_w = 89 (69,100)
		P_m = 82 (42,88)		P_m = 89 (-55,96)
>50,000	16	P_a = 55 (31,78)	8	P_a = 63 (-8,100)
		P_w = 90 (81,98)		P_w = 93 (81,100)
		P_m = 67 (21,92)		P_m = 93 (-33,99)
All	59	P_a = -124 (-410,100)	27	P_a = 65 (38,91)
		P_w = 74 (69,88)		P_w = 91 (83,98)
		P_m = 54 (29,82)		P_m = 91 (79,95)

[a]Numbers in parentheses are approximate 95 percent confidence interval for the percent emission reductions.

P_a = Average percent reduction, where percent reduction = $\dfrac{100 \times (\text{emission rate before maintenance} - \text{emission rate after maintenance})}{\text{emission rate before maintenance}}$

P_w = Weight percent reduction = $\dfrac{\sum \text{emission rate before maintenance} - \sum \text{leak rate after maintenance}}{\sum \text{emission rate before maintenance}} \times 100$

P_m = Median percent reduction

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The complete report is in five volumes, entitled "Assessment of Atmospheric Emissions from Petroleum Refining:"
Volume 1. Final Report (Order No. PB 80-225 253; Cost: $33.50)
Volume 2. Appendix A - Methodology (Order No. PB 80-225 261; Cost: $17.00)
Volume 3. Appendix B - Detailed Results (Order No. PB 225-279; Cost: $38.00)
Volume 4. Appendix C - Quality Assurance Procedures and Statistical Analysis of Emission Data; Appendix D - Detailed Environmental Assessment; Appendix E - Control Technology Review and Evaluation (Order No. PB 81-103830; Cost: $36.50)
Volume 5. Appendix F - Refinery Technology Characterization (Order No. PB 80-225 287; Cost: $29.00)
All the above reports will be available from: (costs subject to change)
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