

Review of Air Toxics Emission Calculations From Storage Tanks (Phase I)

Air Toxic Emissions Calculation Validation Program: Analysis of Crude Oil and Refined Product Samples and Comparison of Vapor Composition to Model Predictions (Phase II)

API PUBLICATION 2525
DECEMBER 1992

American Petroleum Institute
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Washington, D.C. 20005



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FOREWORD

Phases I and II of this report were contracted to Radian Corporation by the American Petroleum Institute. The purpose of Phase I was to review and assess the validity of the methodology proposed by the Environmental Protection Agency (EPA) for estimating toxic species emissions from storage tanks. The purpose of Phase II was to investigate the validity of assuming ideal liquid behavior (i.e., Raoult's Law) in predicting hazardous air pollutant emissions from petroleum storage tanks. (Phase I, *Review of Air Toxics Emission Calculations from Storage Tanks* was prepared September 1990. Phase II, *Air Toxic Emissions Calculation Validation Program: Analysis of Crude Oil and Refined Product Samples and Comparison of Vapor Composition to Model Predictions* was prepared June 1992.)

Based on these two studies, the API's Committee on Evaporation Loss Measurement (CELM) concluded the following:

- EPA's methods for estimating VOC emissions from storage tanks are generally consistent with the generally accepted methods presented in API standards and in EPA's AP-42.
- Raoult's Law can be used to accurately predict vapor phase compositions from liquid composition data.

Phase I initially reviewed EPA's proposed methodology, as presented in *Estimating Air Toxics Emissions from Organic Liquid Storage Tanks* (EPA-450/4-88/004, 1988), as well as methods used in API publications *Evaporative Loss from External Floating-Roof Tanks* (Publication 2517, third edition, 1989), *Evaporation Loss from Fixed-Roof Tanks* (Publication 2518, reaffirmed 1987), and *Evaporation Loss from Internal Floating-Roof Tanks* (Publication 2519, third edition, 1983), and EPA's *Air Emissions Species Manual* (EPA-450/2-88-003a, 1988). The second task of Phase I was to perform an assessment of the validity of EPA's proposed approach for predicting vapor compositions from liquid composition data using Raoult's Law versus more rigorous methods based on equations of state.

Phase I concluded the following:

- EPA's methods for estimating total VOC emissions from storage tanks, as presented in the MRI Report, were generally consistent with the generally accepted methods presented in API publications.
- Results from the use of Raoult's Law to predict vapor phase compositions from liquid composition data were comparable to results from equation of state models, for the gasoline data used in the validation study.
- Use of Raoult's Law to predict vapor phase compositions from liquid composition data yielded results that were comparable to those obtained by using more sophisticated equation of state models.
- Additional data for stocks other than gasoline should be obtained to further test the validity of these models.

Phase II of the Radian study investigated the validity of assuming ideal liquid behavior (Raoult's Law) in predicting hazardous air pollutant emissions from petroleum storage tanks. API members provided Radian with samples of three crude oils (Mid-Continent, Alaska North Slope, and Alaska North Slope spiked with natural gas liquids) and two refined products (JP-4 aviation fuel and No. 2 fuel oil). Liquid and equilibrium vapor samples were analyzed for a suite of twelve selected species; liquid and vapor molecular weights were also measured.

Phase II concluded the following:

- The samples appear to be representative of crude oils and refined products that were sampled (Mid-Continent, Alaska North Slope and ANS spiked with natural gas liquids).
- The data quality objectives established before performing molecular weight and species concentrations on vapor and liquid analyses were met or exceeded for the majority of species analyzed.
- More precise and accurate measurements are possible for liquid samples than vapor sam-

ples. If this can be extrapolated to field measurements, more accurate estimates of air toxics emissions may be possible by predicting vapor compositions based on liquid phase concentration measurements rather than vapor concentration measurements.

- The two equations of state selected for use in this project, Redlich-Kwong-Soave and Peng-Robinson, resulted in predicted vapor concentrations based on the use of measured liquid composition data that were, on average, 5 to 18 percent higher than those resulting when Raoult's Law and the ideal gas law are used. These differences were within the expected confidence intervals computed using the precision and accuracy of the analytical techniques used. There does not appear to be any strong advantage to be gained from use of the more complex models versus Raoult's Law.

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Suggested revisions are invited and should be submitted to the director of the Industry Services Department, American Petroleum Institute, 1220 L Street, N.W., Washington, D.C. 20005.

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1.0 INTRODUCTION

This report presents the results of a study performed by Radian Corporation for the American Petroleum Institute (API). The purpose of this study was to review and assess the validity of the methodology proposed by EPA for estimating emissions of toxic species from storage tanks.

This project involved two tasks:

- Review EPA's proposed methodology for estimating air toxic emissions from organic liquid storage tanks and prepare a summary of findings for review by the API Evaporative Loss Committee; and
- Assess the validity of the calculational methods proposed, including comparisons of calculated results with measured values if possible.

EPA's proposed methodology was presented in report by Midwest Research Institute entitled "Estimating Air Toxics Emissions from Organic Liquid Storage Tanks." (EPA-450/4-88/004, October 1988.) Other principal sources reviewed in Task 1 included the following:

- "Evaporative Loss from External Floating-Roof Tanks," API Publication 2517, Third Edition, February 1989;
- "Evaporation Loss from Fixed-Roof Tanks," API Publication 2518, Reaffirmed August 1987;
- "Evaporation Loss from Internal Floating-Roof Tanks," API Publication 2519, Third Edition, June 1983; and

- "Air Emissions Species Manual," Volume I, VOC Species Profiles, EPA-450/2-88-003a, April 1988.

The procedures for calculating emissions of toxic species presented in the Midwest Research Institute report for EPA were compared with those in the API Publications. Differences were noted, and the validity of the assumptions used in developing the equations and models used was reviewed. The results of this review, including potential methods of validating the procedures, were presented to the members of the API Evaporative Loss Committee in an interim report dated February 27, 1990. The report was discussed with the members of the committee on March 20, 1990, and the proposed validation procedures for Task 2 were approved.

Based on discussions with the committee, the principal focus of Task 2 was to determine the validity of EPA's proposed approach for predicting vapor compositions from liquid composition data using Raoult's Law versus more rigorous methods based on equations of state. Predictions for two gasolines having different volatilities were performed using two equations of state (i.e., Peng-Robinson and Redlich-Kwong-Soave) and Raoult's Law using the ASPEN/SP process simulator.

This report presents the results of the two project tasks. Section 2.0 presents the results of the review of EPA's estimation method. Section 3.0 discusses several potential alternate approaches for estimating air toxics emissions from storage tanks. The results of the validity assessment task are presented in Section 4.0. Section 5.0 is a discussion of conclusions and recommendations, while Section 6.0 is a list of references used in performing the study.

2.0 RESULTS OF METHOD REVIEW

EPA's methodology for estimating air toxic emissions from storage tanks is reviewed in this section. Section 2.1 briefly summarizes EPA's estimation procedures. Section 2.2 provides review comments on the procedures for estimating total emissions. Comments on the methods for estimating emissions of individual air toxics are given in Section 2.3.

2.1 Summary of EPA's Estimation Procedures

The emission estimation methodology presented in the Midwest Research Institute (MRI) report involves the following steps:

1. Determine tank type. The MRI report presents equations for fixed-roof, external floating-roof, and internal floating-roof tanks.
2. Determine estimating methodology. The MRI report provides three suggested approaches for determining the vapor pressure of the stored liquid: (1) read from a table; (2) calculate using Raoult's Law if the mixture can be considered ideal; or (3) measure by sampling and analyzing the vapor. The report suggests that liquid-phase concentrations, needed for making predictions based on Raoult's Law, are "known or can be easily calculated."
3. Select Equations to be Used. The equations for total evaporative loss presented in the MRI report were taken from EPA publication AP-42 (1985 edition) for each of the three tank types.

4. Calculate Liquid Mole Fractions. The MRI report indicates that this step is required only if the liquid's vapor pressure is being estimated using Raoult's Law. The report assumes that the mass fractions of the constituents in the liquid are known; mole fractions can then be calculated by knowing the molecular weights of the constituents.
5. Calculate Partial Pressures and Total Liquid Vapor Pressure. As for Step 4, the MRI report states that this step is needed only when the vapor pressure of the stored liquid is not known. The report presents tabulated vapor pressures at several temperatures for a number of pure organic compounds. The validity of Raoult's Law only for ideal mixtures is reiterated.
6. Calculate Vapor Phase Mole Fractions. This step is required only when vapor component weight fractions or the molecular weight of the vapor are not known. The procedure for an ideal vapor mixture is presented.
7. Calculate Molecular Weight of the Vapor. This step is required only if this quantity is not known. It is calculated by using the molecular weights of the vapor phase constituents and their mole fractions.
8. Calculate Weight Fractions of the Vapor. Again, this step is required where the vapor component weight fractions are not known. The MRI report refers the user to EPA VOC species data manuals for "many mixtures." A general procedure based on vapor phase mole fractions is presented.
9. Calculate Total VOC Emitted from the Tank. This is done using the equations introduced in Step 3, together with parameters calculated in Steps 4 through 8.

10. Calculate Amount of Each Component Emitted. The total VOC emission rate is multiplied by the individual component weight fractions in the vapor (as determined in Step 8).

2.2 Comments on Procedures for Estimating Total Emissions

The procedures for estimating total emissions presented in the MRI report are based on the use of equations from EPA's Publication AP-42. The sources of the equations in AP-42, in turn, are API Publications 2517 (External Floating-Roof Tanks), 2518 (Fixed-Roof Tanks), and 2519 (Internal Floating-Roof Tanks). During the review, the equations presented in the report were compared with those in the most recent version of AP-42 (September 1985), and those in the most recent releases of the API publications.

For the most part, the equations in the MRI report were found to be equivalent to those in the API publications. AP-42 and the report extend the use of the equations from gasoline and crude oil to all organic liquids.

A number of discrepancies were noted during the review. These are discussed below.

Fixed Roof Tank Breathing Loss

The equation presented in the MRI report for fixed roof tank breathing loss estimation is similar to that found in API-2518, with a few exceptions. First, the vapor pressure function has been generalized to allow for atmospheric pressure levels other than 14.7 psia. Second, the temperature at which the vapor pressure of the stored liquid is calculated is given as a function of the paint color in the report, and varies from a temperature equal to the ambient temperature for white tanks to the ambient temperature plus 5°F for black tanks. API-2518 merely suggests adding 5°F to the ambient

temperature regardless of the tank color. It is expected that this difference will not result in major differences in the total estimated emissions for most cases.

Because of the choice of units, the equation in the MRI report includes the molecular weight of the vapor, M_v . Note that the equation for estimating M_v presented on page 26 of the MRI report implicitly assumes the validity of Raoult's Law.

A major discrepancy was found in the value of the numerical coefficient in the equation for breathing losses from fixed-roof tanks. The coefficient given in the MRI report, which provides estimated emissions in units of lb/year, is the same as that in the 1985 edition of AP-42 (i.e., 0.0226). When converted to the same basis, the coefficient given in the earlier edition of AP-42 (April 1977) would be 0.0807, which means that its use would result in a breathing loss estimate about 3.6 times that obtained when using the more recent version of AP-42. This point was discussed with the members of the API Evaporative Loss Committee, who indicated that recent API data confirms the lower total emission rate for vapor pressures less than 2 psi. The next revision of API-2518 will incorporate these data, possibly by using a different vapor pressure function.

Another discrepancy was noted in the value of the crude oil product factor, K_c . The value in the MRI report, 0.65, is consistent with that presented in both 1977 and 1985 editions of AP-42; API-2518 suggests the use of 0.58 for this factor. The reason for the difference is not known.

The curve showing the small tank adjustment factor, C , as a function of tank diameter has been extrapolated to the origin in the MRI report, as was done in AP-42.

Finally, the table of paint factors (F_p) as a function of tank color and paint condition uses the same numerical values as in API-2518, but adds

values for light and medium gray paint in poor condition by extrapolation. This is done by multiplying by the average ratio of poor/good condition factors for the paint colors presented earlier in the table.

Fixed-Roof Tank Working Loss

The form of the equation presented in the MRI report is equivalent to that found in API-2518, assuming the validity of the relationship discussed above for converting bbl/year to lb/year.

There are discrepancies in the value of the crude oil product factor, K_c , used in the report (0.65), versus AP-42 (0.84), and API-2518 (0.75). The reason for these differences is not known.

Horizontal Fixed Roof Storage Tanks

The MRI report contains a paragraph (p. 28) on adapting the equations presented for vertical fixed-roof tanks to the estimation of emissions from horizontal tanks. The statement is made that the method suggested gives "only a very approximate" value for emissions from horizontal fixed-roof tanks. It was not possible to assess the validity of the procedures presented for estimating emissions from such tanks.

External Floating Roof Tanks

The equations presented in the MRI report for estimating rim seal and roof fitting losses (combined in AP-2517 as the Standing Storage Loss and Withdrawal Loss) for external floating roof tanks are consistent with equations given in API-2517. The only major discrepancy between the report and API-2517 was the default value of the average liquid density of gasoline.

The report gives 5.6 lb/gal, while API-2517 (p. 15) suggests the use of 6.1 lb/gal.

The report's discussion of withdrawal loss from external floating roof tanks is complicated unnecessarily by the introduction of a factor that is applicable only to internal floating roof tanks. In general, the report tries to avoid duplication by including equations that are applicable to both external and internal floating roof tanks in the section on external floating roof tanks alone. This causes the reader to have to flip back and forth in the text, which seems awkward.

With the exception of a few typographical errors, there were no other differences between the MRI report and API-2517.

Internal Floating Roof Tanks

The equations presented in this section of the MRI report are identical to those in API-2519. The same comments given earlier with respect to estimation of vapor molecular weight, M_v , and the discrepancy in the default value of gasoline density apply to this type of tank, since the report refers to notes already discussed in previous sections of this review.

2.3 Comments on Procedures for Estimating Emissions of Individual Air Toxics

Emissions of individual air toxics are estimated based on multiplying total emissions, in units of mass per unit time, by the vapor phase mass fraction of each species. The vapor mass fractions can, in turn, be calculated from vapor phase mole fractions and species molecular weights. The MRI report provides three methods of determining vapor phase mass or mole fractions:

- Read from a table;
- Measure by sampling and analyzing the vapor; and
- Calculate from liquid composition using Raoult's Law

The following paragraphs briefly discuss each of these options.

Using Tabulated Values. This alternative would be most useful if no liquid or vapor composition data were available for specific petroleum stocks. Reading values of vapor composition from a table would certainly be an easy approach, assuming that such data could be found for the specific liquid being stored. EPA's VOC Species Profiles (Shareef et al. 1988), cited in the MRI report, are one such source of data. Vapor compositions are given for commercial jet fuel, crude oil, and gasoline (summer and winter blends). However, an examination of the data shows that they present very limited or no information on air toxics species, and in some cases were derived not from measurements but by an "engineering evaluation of literature data." The use of these data to predict air toxics emissions for specific refinery stock and products may not produce very accurate estimates.

Sampling and Analysis. The determination of vapor compositions by sampling and analysis represents the other extreme. It is attractive from the standpoint of being able to provide composition data that are directly applicable to specific cases. However, it, too, suffers from some drawbacks, including logistical difficulties (e.g., sampling the vapor from a floating-roof tank) and analysis costs. Difficulties may also arise because the composition of the vapor above a mixture changes with temperature, so the data represent a "snapshot" of the emissions at a specific set of conditions, not necessarily those at which average emissions are to be calculated. Stratification may also present difficulties in obtaining a representative vapor sample.

Raoult's Law Estimation. The use of Raoult's Law assumes that liquid phase composition data are available. Raoult's Law provides a way of estimating the composition of the vapor based on the liquid composition. It may be stated mathematically as follows:

$$y_i = P_i x_i / P_T$$

where y_i = mole fraction of component i in the vapor;

P_i = vapor pressure of component i ;

x_i = mole fraction of component i in the liquid; and

P_T = total pressure. For an ideal vapor mixture, the total pressure is simply the sum of the partial pressures of the species present.

The MRI report points out that Raoult's Law is valid only for ideal liquid mixtures. It suggests that the behavior of mixtures whose components have similar molecular structures and molecular weights can be assumed to be nearly ideal. It specifically cautions against the use of Raoult's Law with complex mixtures of hydrocarbons such as "petroleum stocks." A list of common organic functional groups leading to non-ideal solutions is provided (p. 23). These caveats are reiterated several places in the report, although there are places where the equations provided are based implicitly on the validity of Raoult's Law without the caveat. For example, on page 26, the equation for estimating the molecular weight of the vapor, M_v , relates the liquid phase composition, component vapor pressures, and total pressure in terms of Raoult's Law.

2.4 Conclusions

The following summarizes the conclusions from Radian's review of the MRI Report "Estimating Air Toxics Emissions from Organic Liquid Storage Tanks":

- With a few specific exceptions, the MRI report provides an approach to estimating overall storage tank emissions that is generally consistent with the generally accepted methodology published earlier in EPA's AP-42 and various API publications. The specific discrepancies have been discussed above.
- To estimate emissions of individual air toxics, the report suggests the use of published data (e.g., VOC Species Profiles), measured vapor compositions, or, under the assumption that the liquid behavior can be assumed to be close to ideal, the use of Raoult's Law. Whether or not Raoult's Law can be used to predict vapor compositions over stored liquids of interest to the petroleum refining industry is a question that needs to be resolved.

The next section of this report discusses potential alternatives to Raoult's Law for estimating vapor compositions needed to estimate emissions of specific components from storage tanks containing crude oil and petroleum products, with emphasis on air toxics.

3.0 ALTERNATE APPROACHES FOR ESTIMATING AIR TOXICS EMISSIONS

This section discusses the pros and cons of several alternate approaches for estimating vapor phase compositions from liquid composition data.

3.1 Henry's Law

Raoult's Law is an example of a special case where the liquid- and vapor-phase mole fractions of a species are related through the use of a constant. Henry's Law can be viewed as a general form of this relationship:

$$y_i = H_i x_i / P_T$$

where H_i = Henry's Law constant for component i .

Henry's Law has been shown to give good results for solutes present in low concentrations in a solvent. This would certainly be the situation for toxic organic compounds present in trace concentrations in an organic liquid mixture.

However, most of the Henry's Law constants available in the open literature have been developed for dissolved gases in aqueous systems. Henry's Law constants for organics dissolved in other organics, such as petroleum stocks and products, may not be readily available. Developing these constants would require a major research effort that would be difficult to justify if other alternatives can be found that use more readily available data.

3.2 Petroleum K-Values

Data have been available for many years relating vapor and liquid compositions as a function of temperature and pressure for a number of light organic compounds and pseudo-compounds (e.g., boiling-point cuts) found in petroleum refining applications. The form of the relationship is as follows:

$$y_i = K_i x_i$$

where K_i = K-value for i .

K-values are available in the form of nomographs or as regressions based on temperature and pressure.

Unfortunately, the majority of the air toxics species of interest are not included in the list of components for which K-values have been developed. In addition, the ranges of temperature and pressure included in the correlations are typically higher than those likely to occur in storage tanks, since their principal use has been in estimating fractionation behavior in distillation columns.

Developing the necessary K-value data for storage tank conditions and for the species of interest could require a major research effort.

3.3 Activity Coefficients

If the vapor phase can be considered to behave as an ideal gas mixture, then activity coefficients may be viewed as correction factors to Raoult's Law that take liquid-phase non-idealities into account in relating vapor- and liquid-phase compositions:

$$y_i = \gamma_i P_i x_i / P_T$$

where γ_i = activity coefficient for component i.

A number of different models have been developed for estimating activity coefficients. Examples include the VanLaar, Margules, Scatchard-Hamer, and Wilson equations. Activity coefficients for binary mixtures typically include factors that account for intermolecular interactions between the two species present in the mixture. These factors typically depend on the mole fractions of both species; the values of the constants depend on the particular model being used. In mixtures having more than two components, activity coefficients must be obtained for each possible pair of components and then combined using "mixing rules."

Determination of the constants for each binary pair would obviously become extremely costly for complex mixtures such as refinery stocks.

3.4 Equations of State

The use of suitable equations of state is attractive since they can account for non-ideal behavior in both vapor and liquid phases. Their implementation for complex mixtures can be readily handled by the use of computers.

A number of computerized design software packages have been developed (e.g., ASPEN) that have the capability of estimating vapor-liquid equilibrium (VLE) for mixtures containing a large number of components. These VLE routines typically allow the user to select from among several options, all the way from ideal gas and liquid mixtures to sophisticated equation of state techniques that account for non-idealities in both liquid and vapor phases.

The use of these software packages has increased dramatically in the past few years. Most of the large petroleum refining companies undoubtedly have access to one or more of them. Some companies have probably developed their own, incorporating proprietary VLE data. It appears that a viable option for these companies might be to utilize the capabilities of these tools as an aid in estimating air toxics emissions from their storage tanks.

4.0 VALIDITY ASSESSMENT

After discussing the options presented in the previous section with the members of API's Evaporative Loss Committee, it was decided to assess the validity of using equations of state as alternatives to the use of Raoult's Law for predicting vapor compositions from liquid phase data.

The validity assessment task included the following steps:

- Obtain liquid and vapor composition data from the literature for stocks of interest, including gasolines, crude oil, and others, if available.
- Use these data as input to the ASPEN/SP process simulator to develop predicted vapor compositions, using Raoult's Law and more sophisticated equations of state.
- Compare the predictions based on the use of Raoult's Law and the equations of state against the literature vapor composition data.

Radian located liquid and vapor composition data for several different gasolines (Wright, Menon, and Peoples, 1989). Unfortunately, such data were not found for other stocks of interest. Data for summer and winter blend unleaded regular gasolines were used in the assessment.

The species of particular interest to API were the toxic components that refiners may potentially need to report under the provisions of Section 313 of the Superfund Amendments and Reauthorization Act (SARA). A list of the components of potential concern was provided by P. C. Tranquill, and is included as Table 4-1. An asterisk is shown next to those toxic species included in the vapor composition data given in the Volatile Organic Compound Species Profiles (Section 3.20: Storage, Transportation, and Marketing

TABLE 4-1. LIST OF COMPONENTS POTENTIALLY REPORTABLE BY REFINERS
UNDER SARA TITLE III, SECTION 313

Aniline
 Anthracene
 * Benzene
 Cresol (mixed isomers)
 m-Cresol
 o-Cresol
 p-Cresol
 * Cumene
 * Cyclohexane
 Dibenzofuran
 Diethanolamine
 2,4-Dimethylphenol
 * Ethylbenzene
 Ethylene glycol
 Ethylene
 Methanol
 Methyl tert-butyl ether
 Methyl ethyl ketone
 Methyl isobutyl ketone
 * Naphthalene
 p-Phenylenediamine
 Phenol
 Phosgene
 Propylene
 Pyridine
 Quinoline
 Styrene
 * Toluene
 o-Toluidene
 * 1,2,4-Trimethylbenzene
 * Xylene (mixed isomers)
 m-Xylene
 * o-Xylene
 p-Xylene
 2,6-Xylidine

Source: Transmission from P.C. Tranquill, BP Oil Company

* Present in vapor-phase data in EPA Volatile Organic Compound Species Profiles, Section 3.20 (Storage, Transportation, and Marketing of Petroleum Products) or gasoline vapor data provided in Wright, Menon, and Peoples (1989).

of Petroleum Products) and the gasoline vapor data in Wright, Menon, and Peoples (1989).

4.1 Methodology for Estimating Vapor Compositions

The ASPEN/SP simulator's Two-Phase Flash model was used to predict the composition of the vapor in equilibrium with liquid gasolines with the compositions presented in Wright, Menon, and Peoples. Input data required by the simulator included a list of the components and their "aliases" (the names under which the various physical and chemical property data are stored in the program's databanks); the specific data banks to access for each component (since data for all of the components were not available in a single data bank); the inlet liquid concentration data; and the temperature and vapor fraction to use in the flash calculation.

A few species present in the gasolines were not included in any of ASPEN's physical properties databanks. For these species, surrogates having similar molecular weights and boiling points were chosen. Adequate data were available in the ASPEN/SP data banks for all of the air toxics species of interest.

In addition to Raoult's Law, two different equations of state were used to model the VLE behavior of the gasolines selected: Peng-Robinson and Redlich-Kwong-Soave. These equations were chosen since they have previously been shown to predict accurately the behavior of hydrocarbon systems.

4.2 Discussion of Results

The results of the ASPEN/SP runs are summarized in Tables 4-2 and 4-3 for the two gasolines. The tables show the measured and predicted vapor-phase concentrations of the air toxic species, measured and predicted vapor

TABLE 4-2. SUMMARY OF RESULTS FOR SUMMER BLEND UNLEADED GASOLINE

Toxic Species	Measured ¹		Predicted Vapor Concentration		
	Liquid	Vapor			
	wt%	wt%	Raoult ²	P-R EOS ³	R-K-S EOS ⁴
Cyclohexane	0.58	0.20	0.25	0.27	0.26
Benzene	1.93	0.73	0.83	1.05	0.99
Toluene	10.32	0.81	1.29	1.57	1.45
O-Xylene	3.39	0.05	0.00	0.00	0.00
Isomers of Xylene	9.16	0.21	0.31	0.33	0.30
Ethylbenzene	2.05	0.05	0.00	0.00	0.00
Isopropylbenzene	0.19	--	0.00	0.00	0.00
1,2,4-Trimethylbenzene	3.52	0.04	0.00	0.00	0.00
Molecular Weight of Vapor		67.6	67.0	67.4	67.2
Predicted Vapor Pressure			3.92	4.04	4.00
Relative Concentration Errors:					
Average for all Species			4.0%	10.4%	7.3%
Average for Toxics			22.7%	36.5%	29.6%
Absolute Value for all Species			16.7%	22.2%	19.5%
Absolute Value for Toxics			22.7%	36.5%	29.6%

¹Source: Wright, Menon, and Peoples (1989)²Raoult = Raoult's Law³P-R EOS = Peng-Robinson Equation of State⁴R-K-S EOS = Redlich-Kwong-Soave Equation of State

TABLE 4-3. SUMMARY OF RESULTS FOR WINTER BLEND UNLEADED GASOLINE

Toxic Species	Measured ¹		Predicted Vapor Concentration		
	Liquid	Vapor			
	wt%	wt%	Raoult ²	P-R EOS ³	R-K-S EOS ⁴
Cyclohexane	0.50	0.34	0.16	0.17	0.16
Benzene	1.82	1.43	0.56	0.71	0.67
Toluene	9.11	2.10	0.82	1.00	0.92
O-Xylene	3.59	0.51	0.00	0.00	0.00
Isomers of Xylene	8.75	1.02	0.21	0.23	0.00
Ethylbenzene	2.08	0.31	0.00	0.00	0.00
Isopropylbenzene	0.19	--	0.00	0.00	0.00
1,2,4-Trimethylbenzene	4.21	0.05	0.00	0.00	0.00
Naphthalene	0.25	--	0.00	0.00	0.00
Molecular Weight of Vapor		68.9	63.6	63.9	63.7
Predicted Vapor Pressure			5.60	5.76	5.74
Relative Concentration Errors:					
Average for all Species			-22.9%	-22.4%	-20.5%
Average for Toxics			-21.6%	-19.4%	-10.7%
Absolute Value for all Species			34.0%	33.1%	31.4%
Absolute Value for Toxics			33.6%	31.4%	24.7%

¹Source: Wright, Menon, and Peoples (1989)²Raoult - Raoult's Law³P-R EOS - Peng-Robinson Equation of State⁴R-K-S EOS - Redlich-Kwong-Soave Equation of State

molecular weight, and predicted vapor pressure (at a temperature of 60°F). Overall average errors relative to the measured concentrations for the toxic components as well as all components are also provided. More detailed species-by-species comparisons are included in the Appendix.

Summer Blend Gasoline

The air toxics results for the summer blend gasoline are shown graphically in Figure 4-1. As can be seen, there are no significant differences between the predictions using Raoult's Law and the two equations of state for this product. All three methods predicted vapor phase concentrations somewhat higher than the measured concentrations.

The impact of a different assumed temperature on the vapor concentrations predicted using Raoult's Law is shown in Figure 4-2. The temperature of 60°F was chosen since it minimized the overall average error between predicted and reported vapor compositions.

Winter Blend Gasoline

Figure 4-3 shows the predicted versus reported concentrations for the air toxics compounds for the winter blend gasoline case. As had been observed for the summer blend gasoline, there were no significant differences between the predictions using Raoult's Law and the two equations of state. In this case, the models predicted vapor concentrations that were all lower than the reported values.

The predicted concentrations shown were all based on an assumed temperature of 60°F. The impact of increased temperature on the predicted air toxics concentrations can be seen in Figure 4-4, where the predictions based

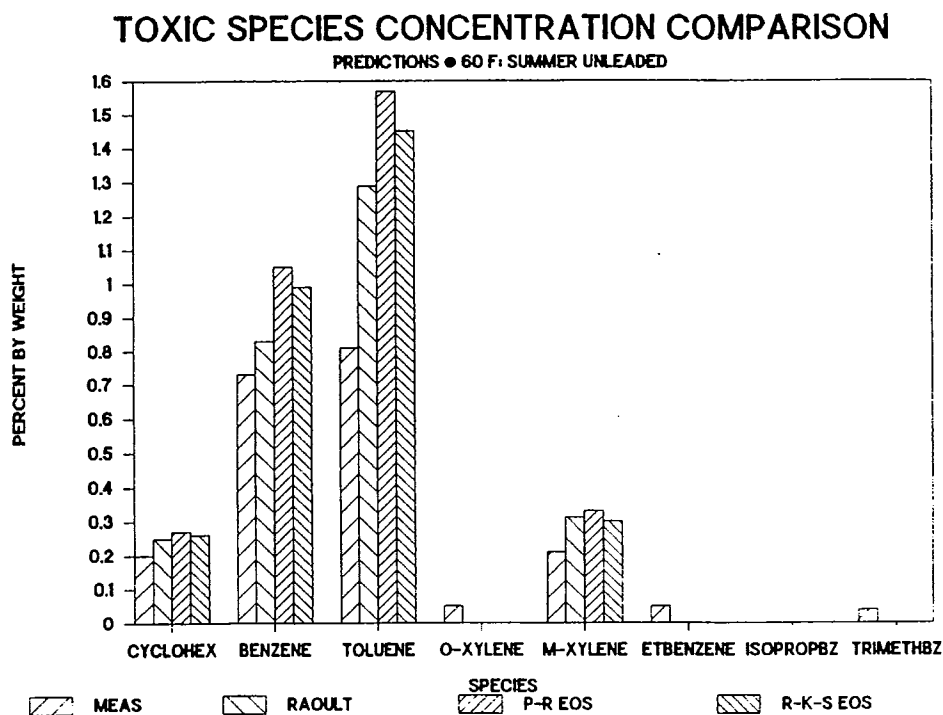


Figure 4-1. Measured Versus Predicted Vapor-Phase Air Toxics Concentrations for Summer Blend Unleaded Gasoline

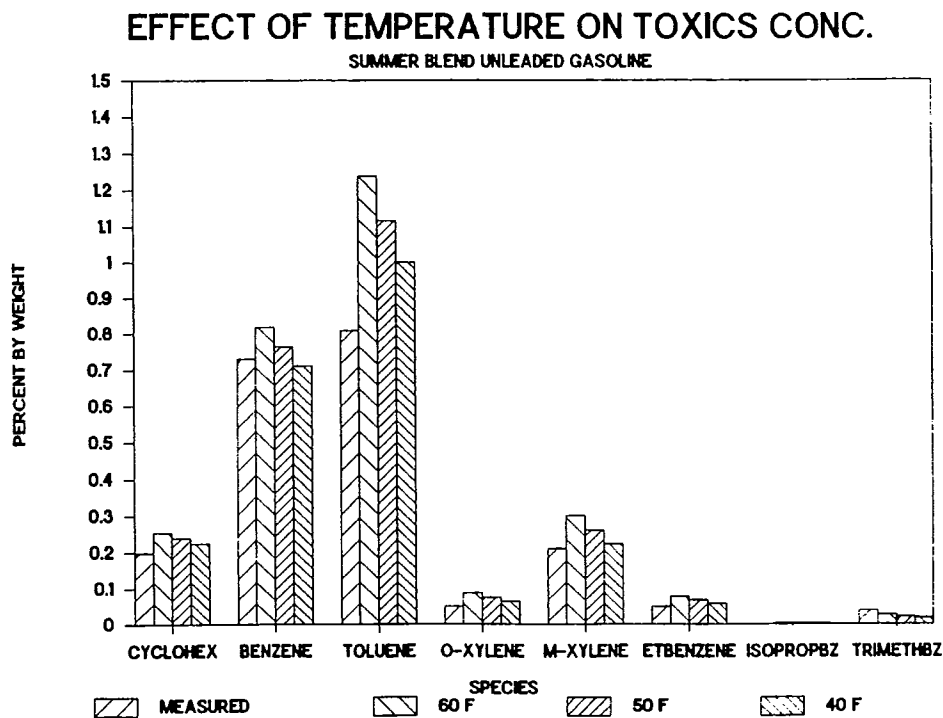


Figure 4-2. Impact of Assumed Temperature on Vapor-Phase Air Toxics Concentrations for Summer Blend Gasoline

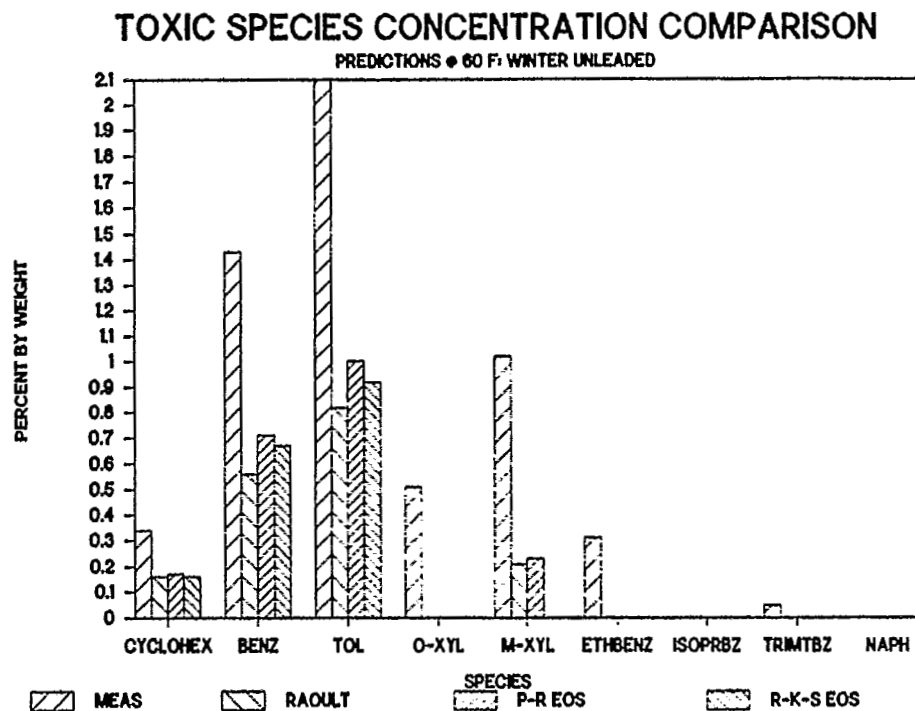


Figure 4-3. Measured Versus Predicted Vapor-Phase Air Toxics Concentrations for Winter Blend Unleaded Gasoline

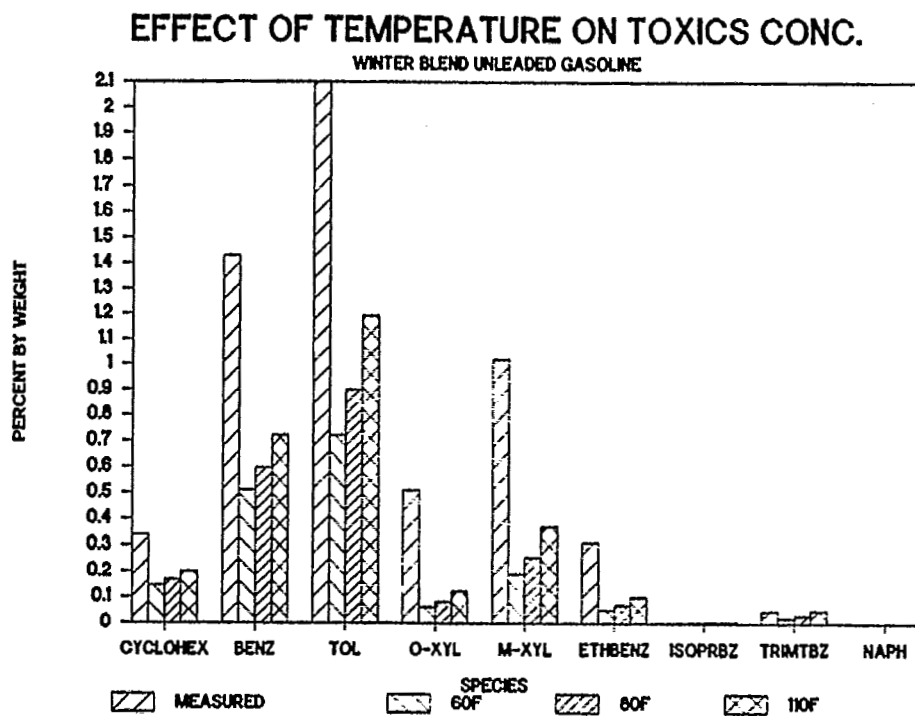


Figure 4-4. Impact of Assumed Temperature on Vapor-Phase Air Toxics Concentrations for Winter Blend Gasoline

on Raoult's Law are compared to the measured values. Increasing the assumed temperature decreased the difference between the reported and predicted concentrations, but a significant difference was still seen even as the assumed temperature approached the bubble point of the gasoline, about 115°F.

4.3 Limitations

The discussion of relative error presented above naturally assumes that there were no measurement errors associated with the reported liquid and vapor concentrations, and that the sampled vapor was in true equilibrium with the liquid. It is likely that neither of these assumptions was totally valid. Given the potential for uncertainty in the reported concentrations, the predictions of all three models appear to be reasonably good.

The tentative conclusion from the limited validation assessment performed is that the use of Raoult's Law in the prediction of vapor compositions from liquid composition data gives essentially the same level of accuracy as those based on more sophisticated equations of state, at least for the gasolines included in the assessment.

Unfortunately, it is not possible to generalize these results to other stocks of interest, such as crude oils, since the validation did not include them. It would be advisable to perform additional validation tests for crude oils in particular, because of their complexity and the presence of compounds that are known to lead to non-ideal solution behavior.

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study resulted in the following conclusions:

- With a few exceptions, the methods for estimating total VOC emissions from storage tanks presented in the MRI Report were found to be equivalent to generally accepted methods presented in API Publications.
- The use of Raoult's Law to predict vapor phase compositions from liquid composition data gave results comparable to those obtained using more sophisticated equation of state models, for the gasoline data used in the validation study.
- For gasoline storage, fairly good estimates of air toxic emissions can probably be obtained by using either Raoult's Law or the equations of state. Since the same amount of effort is involved in using either method, the more sophisticated technique is recommended if a company has access to a process simulator. If this is not the case, a computer spreadsheet based on Raoult's Law would be simple to develop and would probably provide adequate results for Title 313 reporting purposes, at least for gasoline storage tanks.
- Additional data for other stocks, especially crude oils, should be obtained to further test the validity of these vapor/liquid equilibrium models.

5.2

Recommendations

- Additional effort should be given to locating vapor and liquid data for additional stored liquids, including crude oils. Predictions based on Raoult's Law and equations of state should be performed using these data.
- If such data cannot be located, there are several options available for developing them. The simplest would be obtain liquid samples for use in a laboratory vapor-liquid equilibrium study. After the samples had been allowed to come to equilibrium in a constant-temperature bath, vapor and liquid samples would be withdrawn and analyzed using GC/MS techniques. The results could then be compared to predictions from various models.
- Another option would be to conduct a field sampling and analysis program in which vapor and liquid samples from tanks containing crude oil and products of interest. Such a program could also be used as a logical follow-on to the laboratory-scale work described above. The impacts of liquid stratification and other variables on the observed vapor and liquid compositions could be investigated.

6.0 REFERENCES

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APPENDIX:

Detailed Comparisons of Measured and Predicted Vapor
Compositions for Summer and Winter Blend Gasolines

COMPARISON OF MEASURED VERSUS PREDICTED VAPOR COMPOSITION
BASED ON MEASURED LIQUID COMPOSITIONLIQUID GASOLINE -- UNLEADED REGULAR -- SUMMER BLEND
SOURCE: WRIGHT, MENON, AND PEOPLES, 1989

CHEMICAL NAME	MODELED SPECIES	ASPEN ALIAS	MEASURED	NORMALIZED	VAPOR COMPOSITION PREDICTIONS		
			LIQUID WEIGHT PERCENT	VAPOR WEIGHT PERCENT	RAOULT'S	P-R EOS	R-K-S EOS
N-BUTANE	N-BUTANE	C4H10-1	3.27	27.19	31.10	30.16	30.65
ISO-BUTANE	ISO-BUTANE	C4H10-2	0.76	10.63	10.69	10.50	10.78
ISOMERS OF BUTENE	1-BUTENE	C4H8-1	0.08	1.08	0.93	0.88	0.89
CIS-2-BUTENE	CIS-2-BUTENE	C4H8-2	0.12	1.19	0.99	0.92	0.92
TRANS-2-BUTENE	TRANS-2-BUTENE	C4H8-3	0.12	1.49	1.09	1.02	1.03
CYCLOPENTANE	CYCLOPENTANE	C5H10-1	0.42	0.54	0.63	0.67	0.65
1-PENTENE	1-PENTENE	C5H10-2	0.34	1.06	1.06	1.13	1.12
CIS-2-PENTENE	CIS-2-PENTENE	C5H10-3	0.34	0.92	0.82	0.80	0.79
TRANS-2-PENTENE	TRANS-2-PENTENE	C5H10-4	0.69	1.81	1.70	1.68	1.67
2-METHYL-1-BUTENE	2-METHYL-1-BUTENE	C5H10-5	0.36	1.35	1.08	1.09	1.09
2-METHYL-2-BUTENE	2-METHYL-2-BUTENE	C5H10-6	1.30	2.63	2.92	2.85	2.85
3-METHYL-1-BUTENE	3-METHYL-1-BUTENE	C5H10-7	0.08	0.44	0.36	0.38	0.38
N-PENTANE	N-PENTANE	C5H12-1	2.54	6.86	6.37	6.33	6.32
ISOMERS OF PENTANE	ISOPENTANE	C5H12-2	6.31	24.00	21.64	21.57	21.66
CYCLOPENTENE	1,2-PENTADIENE	C5H8-2	0.19	0.27	0.34	0.35	0.34
*CYCLOHEXANE	CYCLOHEXANE	C6H12-1	0.58	0.20	0.25	0.27	0.26
3-METHYL-T-2-PENTENE	3-METHYL-T-2-PENTENE	C6H12-10	0.17	0.10	0.11	0.14	0.14
4-METHYL-T-2-PENTENE	4-METHYL-T-2-PENTENE	C6H12-12	0.22	0.24	0.22	0.24	0.23
C6 OLEFINS	2,3-DIMETHYL-2-BUTENE	C6H12-14	0.19	0.08	0.10	0.12	0.12
1-HEXENE	1-HEXENE	C6H12-3	0.19	0.30	0.16	0.16	0.16
C-2-HEXENE	C-2-HEXENE	C6H12-4	0.74	0.47	0.51	0.52	0.51
T-2-HEXENE	T-2-HEXENE	C6H12-5	0.61	0.45	0.44	0.48	0.47
METHYLCYCLOPENTANE	METHYLCYCLOPENTANE	C6H12-2	2.35	1.38	1.48	1.46	1.41
3-METHYL PENTANE	3-METHYL PENTANE	C6H14-3	1.98	2.00	1.75	1.76	1.72
HEXANE	HEXANE	C6H14-1	1.95	1.48	1.34	1.40	1.37
2,2-DIMETHYLBUTANE	2,2-DIMETHYLBUTANE	C6H14-4	0.91	1.20	1.39	1.47	1.45
ISOMERS OF HEXANE	2,3-DIMETHYLBUTANE	C6H14-5	3.23	3.88	3.57	3.68	3.62
*BENZENE	BENZENE	C6H6	1.93	0.74	0.83	1.05	0.99
METHYLCYCLOHEXANE	METHYLCYCLOHEXANE	C7H14-6	0.93	0.13	0.19	0.20	0.19
HEPTANE	HEPTANE	C7H16-1	2.06	0.35	0.41	0.42	0.40
ISOMERS OF HEPTANE	2-METHYLHEXANE	C7H16-2	5.67	1.64	1.64	1.76	1.69
3-METHYLHEXANE	3-METHYLHEXANE	C7H16-3	2.03	0.53	0.55	0.57	0.55
2,4-DIMETHYLPENTANE	2,4-DIMETHYLPENTANE	C7H16-6	1.10	0.58	0.48	0.52	0.51
*TOLUENE	TOLUENE	C7H8	10.32	0.82	1.29	1.57	1.45
*O-XYLENE	O-XYLENE	C8H10-1	3.39	0.05	0.00	0.00	0.00
*ISOMERS OF XYLENE	M-XYLENE	C8H10-2	9.16	0.21	0.31	0.33	0.30
*ETHYLBENZENE	ETHYLBENZENE	C8H10-4	2.05	0.05	0.00	0.00	0.00
OCTENE	1-OCTENE	C8H16-16	0.19	--	0.00	0.00	0.00
C8 OLEFINS	C-2-OCTENE	C8H16-17	0.36	0.10	0.00	0.00	0.00
C-2-OCTENE	C-2-OCTENE	C8H16-17	0.17	--	0.00	0.00	0.00



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COMPARISON OF MEASURED VERSUS PREDICTED VAPOR COMPOSITION
BASED ON MEASURED LIQUID COMPOSITIONLIQUID GASOLINE -- UNLEADED REGULAR -- SUMMER BLEND
SOURCE: WRIGHT, MENON, AND PEOPLES, 1989

CHEMICAL NAME	MODELED SPECIES	ASPEN ALIAS	MEASURED	NORMALIZED	VAPOR COMPOSITION PREDICTIONS		
			LIQUID WEIGHT PERCENT	VAPOR WEIGHT PERCENT	RAOULT'S	P-R EOS	R-K-S EOS
OCTANE	N-OCTANE	C8H18-1	1.03	0.05	0.00	0.00	0.00
ISOMERS OF OCTANE	N-OCTANE	C8H18-1	0.80	0.05	0.00	0.00	0.00
2,2,4-TRIMETHYLPENTANE	2,2,4-TRIMETHYLPENTANE	C8H18-13	3.01	0.73	0.63	0.74	0.70
2,3,4-TRIMETHYLPENTANE	2,3,4-TRIMETHYLPENTANE	C8H18-15	1.17	0.12	0.13	0.14	0.13
3-METHYLHEPTANE	3-METHYLHEPTANE	C8H18-3	1.61	0.08	0.13	0.14	0.13
2,5-DIMETHYLHEXANE	2,5-DIMETHYLHEXANE	C8H18-8	1.29	0.15	0.16	0.19	0.18
N-PROPYLBENZENE	N-PROPYLBENZENE	C9H12-1	0.58	--	0.00	0.00	0.00
*ISOPROPYLBENZENE (CUMENE)	ISOPROPYLBENZENE (CUMENE)	C9H12-2	0.19	--	0.00	0.00	0.00
O-ETHYLTOLUENE	O-ETHYLTOLUENE	C9H12-3	1.20	0.04	0.00	0.00	0.00
M-ETHYLTOLUENE	M-ETHYLTOLUENE	C9H12-4	2.88	--	0.00	0.00	0.00
1,2,3-TRIMETHYLBENZENE	1,2,3-TRIMETHYLBENZENE	C9H12-6	0.83	0.04	0.00	0.00	0.00
*1,2,4-TRIMETHYLBENZENE	1,2,4-TRIMETHYLBENZENE	C9H12-7	3.52	0.04	0.00	0.00	0.00
1,3,5-TRIMETHYLBENZENE	1,3,5-TRIMETHYLBENZENE	C9H12-8	1.29	0.02	0.00	0.00	0.00
1-NONENE	1-NONENE	C9H18-3	0.22	--	0.00	0.00	0.00
C9 OLEFINS	1-NONENE	C9H18-3	0.78	--	0.00	0.00	0.00
NONANE	N-NONANE	C9H20-1	0.59	--	0.00	0.00	0.00
ISOMERS OF NONANE	N-NONANE	C9H20-1	2.08	0.04	0.00	0.00	0.00
3,5,5-TRIMETHYLHEXANE	3,5,5-TRIMETHYLHEXANE	C9H20-3	1.62	0.11	0.00	0.15	0.00
2,2,5-TRIMETHYLHEXANE	2,2,5-TRIMETHYLHEXANE	C9H20-4	0.66	0.04	0.00	0.00	0.00
C10 AROMATICS	N-BUTYLBENZENE	C10H14-1	0.69	--	0.00	0.00	0.00
TERT-BUTYLBENZENE	TERT-BUTYLBENZENE	C10H14-4	0.71	--	0.00	0.00	0.00
C10 OLEFINS	1-DECENE	C10H20-5	0.05	--	0.00	0.00	0.00
ISOMERS OF DECANE	N-DECANE	C10H22-1	0.88	0.00	0.00	0.00	0.00
N-DECANE	N-DECANE	C10H22-1	0.22	--	0.00	0.00	0.00
1-UNDECENE	1-UNDECENE	C11H22-2	0.12	--	0.00	0.00	0.00
UNDECANE	N-UNDECANE	C11H24	0.17	--	0.00	0.00	0.00
M-DIETHYLBENZENE	M-DIETHYLBENZENE	C10H14-7	0.56	--	0.00	0.00	0.00
INDAN	1,2,3-TRIMETHYLBENZENE	C9H12-6	0.37	--	0.00	0.00	0.00
2,4,4-TRIMETHYL-1-PENTENE	2,4,4-TRIMETHYL-1-PENTENE	C8H16-15	0.14	0.03	0.00	0.00	0.00
A-PINENE	A-PINENE	C10H16-2	0.08	--	0.00	0.00	0.00
B-PINENE	B-PINENE	C10H16-3	0.19	--	0.00	0.00	0.00
			98.93	100.00	99.79	99.81	99.82



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COMPARISON OF MEASURED VERSUS PREDICTED VAPOR COMPOSITION
BASED ON MEASURED LIQUID COMPOSITIONGASOLINE -- UNLEADED REGULAR -- WINTER BLEND
SOURCE: WRIGHT, MENON, AND PEOPLES, 1989

CHEMICAL NAME	MODELED SPECIES	ASPEN ALIAS	MEASURED	MEASURED	VAPOR COMPOSITION PREDICTIONS		
			LIQUID WEIGHT PERCENT	VAPOR WEIGHT PERCENT	RAOULT'S	P-R EOS	R-K-S EOS
1,1,2-TRICHLOROETHANE	1,1,2-TRICHLOROETHANE	C2H3CL3	0.06	0.06	0	0.00	0.00
ETHANE	ETHANE	C2H6	0	0.05	0	0.00	0.00
PROPANE	PROPANE	C3H8	0	1.24	0	0.00	0.00
N-BUTANE	N-BUTANE	C4H10-1	5.82	26.36	39.8	39.00	39.33
ISO-BUTANE	ISO-BUTANE	C4H10-2	1.88	13.48	19.02	18.90	19.24
ISOMERS OF BUTENE	1-BUTENE	C4H8-1	0.19	1.19	1.59	1.51	1.53
CIS-2-BUTENE	CIS-2-BUTENE	C4H8-2	0.17	0.77	1.01	0.94	0.94
TRANS-2-BUTENE	TRANS-2-BUTENE	C4H8-3	0.17	1.08	1.11	1.05	1.05
CYCLOPENTENE	1,2-PENTADIENE	C5H8-2	0.19	0.24	0.24	0.25	0.24
CYCLOPENTANE	CYCLOPENTANE	C5H10-1	0.50	0.57	0.54	0.58	0.55
1-PENTENE	1-PENTENE	C5H10-2	0.29	0.71	0.65	0.70	0.69
CIS-2-PENTENE	CIS-2-PENTENE	C5H10-3	0.31	0.55	0.53	0.53	0.52
TRANS-2-PENTENE	TRANS-2-PENTENE	C5H10-4	0.54	1.08	0.96	0.95	0.94
2-METHYL-1-BUTENE	2-METHYL-1-BUTENE	C5H10-5	0.35	0.88	0.75	0.77	0.76
2-METHYL-2-BUTENE	2-METHYL-2-BUTENE	C5H10-6	0.96	1.59	1.55	1.53	1.51
3-METHYL-1-BUTENE	3-METHYL-1-BUTENE	C5H10-7	0.10	0.26	0.32	0.34	0.34
N-PENTANE	N-PENTANE	C5H12-1	2.68	4.95	4.83	4.86	4.81
ISOMERS OF PENTANE	ISOPENTANE	C5H12-2	6.46	15.85	15.93	16.07	16.01
*BENZENE	BENZENE	C6H6	1.82	1.43	0.56	0.71	0.67
*CYCLOHEXANE	CYCLOHEXANE	C6H12-1	0.50	0.34	0.16	0.17	0.16
3-METHYL-T-2-PENTENE	3-METHYL-T-2-PENTENE	C6H12-10			0	0.00	0.00
4-METHYL-T-2-PENTENE	4-METHYL-T-2-PENTENE	C6H12-12		0.22	0	0.00	0.00
C6 OLEFINS	2,3-DIMETHYL-2-BUTENE	C6H12-14	0.63	0.61	0.26	0.31	0.30
METHYLCYCLOPENTANE	METHYLCYCLOPENTANE	C6H12-2	2.20	1.90	1.00	0.99	0.95
1-HEXENE	1-HEXENE	C6H12-3	0.32	0.38	0.19	0.20	0.19
C-2-HEXENE	C-2-HEXENE	C6H12-4	0.15	0.15	0.00	0.00	0.00
T-2-HEXENE	T-2-HEXENE	C6H12-5	0.52	0.50	0.27	0.00	0.29
HEXANE	HEXANE	C6H14-1	1.66	1.48	0.83	0.87	0.84
3-METHYL PENTANE	3-METHYL PENTANE	C6H14-3	1.84	1.96	1.16	1.19	1.15
2,2-DIMETHYLBUTANE	2,2-DIMETHYLBUTANE	C6H14-4	0.83	1.03	0.91	0.97	0.96
ISOMERS OF HEXANE	2,3-DIMETHYLBUTANE	C6H14-5	3.19	3.50	2.53	2.65	2.59
*TOLUENE	TOLUENE	C7H8	9.11	2.10	0.82	1.00	0.92
1-METHYLCYCLOHEXENE	METHYLCYCLOHEXANE	C7H14-6	0.44	0.21	0.19	0.20	0.19
METHYLCYCLOHEXANE	METHYLCYCLOHEXANE	C7H14-6	0.85	0.37			
C7 OLEFINS	1-HEPTENE	C7H14-7	0.26				
HEPTANE	N-HEPTANE	C7H16-1	1.53	0.78	0.21	0.23	0.21
ISOMERS OF HEPTANE	2-METHYLHEXANE	C7H16-2	4.43	3.37	0.92	1.00	0.96
3-METHYLHEXANE	3-METHYLHEXANE	C7H16-3	1.59	0.97	0.31	0.32	0.31
2,4-DIMETHYLPENTANE	2,4-DIMETHYLPENTANE	C7H16-6	0.96	0.87	0.30	0.33	0.32



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COMPARISON OF MEASURED VERSUS PREDICTED VAPOR COMPOSITION
BASED ON MEASURED LIQUID COMPOSITIONGASOLINE -- UNLEADED REGULAR -- WINTER BLEND
SOURCE: WRIGHT, MENON, AND PEOPLES, 1989

CHEMICAL NAME	MODELED SPECIES	ASPEN ALIAS	MEASURED	MEASURED	VAPOR COMPOSITION PREDICTIONS		
			LIQUID WEIGHT PERCENT	VAPOR WEIGHT PERCENT	RAOULT'S	P-R EOS	R-K-S EOS
*O-XYLENE	O-XYLENE	C8H10-1	3.59	0.51	0.00	0.00	0.00
*ISOMERS OF XYLENE	M-XYLENE	C8H10-2	8.75	1.02	0.21	0.23	
*ETHYLBENZENE	ETHYLBENZENE	C8H10-4	2.08	0.31	0.00	0.00	
2,4,4-TRIMETHYL-1-PENTENE	2,4,4-TRIMETHYL-1-PENTENE	C8H16-15	0.07	0.06	0.00	0.00	
OCTENE	1-OCTENE	C8H16-16	0.16	0.06		0.00	
C-2-OCTENE	C-2-OCTENE	C8H16-17		0.05	0.00	0.00	
C8 OLEFINS	C-2-OCTENE	C8H16-17	0.39	0.13		0.00	
ISOMERS OF OCTANE	N-OCTANE	C8H18-1	3.10	1.64			
OCTANE	N-OCTANE	C8H18-1	0.83	0.22	0.17	0.18	0.17
2,2,4-TRIMETHYLPENTANE	2,2,4-TRIMETHYLPENTANE	C8H18-13			0.00	0.00	
2,3,4-TRIMETHYLPENTANE	2,3,4-TRIMETHYLPENTANE	C8H18-15	0.74	0.28	0.00	0.00	
3-METHYLHEPTANE	3-METHYLHEPTANE	C8H18-3	1.21	0.41	0.00	0.00	
2,5-DIMETHYLHEXANE	2,5-DIMETHYLHEXANE	C8H18-8	0.93	0.41	0.00	0.00	
N-PROPYLBENZENE	N-PROPYLBENZENE	C9H12-1	0.69		0.00	0.00	
C9 AROMATICS	N-PROPYLBENZENE	C9H12-1	1.60			0.00	
*ISOPROPYLBENZENE (CUMENE)	ISOPROPYLBENZENE (CUMENE)	C9H12-2	0.25		0.00	0.00	
O-ETHYLTOLUENE	O-ETHYLTOLUENE	C9H12-3	1.25	0.02	0.00	0.00	
M-ETHYLTOLUENE	M-ETHYLTOLUENE	C9H12-4	3.25	0.05	0.00	0.00	
INDAN	1,2,3-TRIMETHYLBENZENE	C9H12-6	0.52		0.00	0.00	
1,2,3-TRIMETHYLBENZENE	1,2,3-TRIMETHYLBENZENE	C9H12-6	1.31	0.02	0.00	0.00	
*1,2,4-TRIMETHYLBENZENE	1,2,4-TRIMETHYLBENZENE	C9H12-7	4.21	0.05	0.00	0.00	
1,3,5-TRIMETHYLBENZENE	1,3,5-TRIMETHYLBENZENE	C9H12-8	1.30	0.02	0.00	0.00	
C9 OLEFINS	1-NONENE	C9H18-3	0.41	0.28	0.00	0.00	
1-NONENE	1-NONENE	C9H18-3	0.04		0.00	0.00	
ISOMERS OF NONANE	N-NONANE	C9H20-1	1.35	0.54	0.00	0.00	
NONANE	N-NONANE	C9H20-1	0.57		0.00	0.00	
3,5,5-TRIMETHYLHEXANE	3,5,5-TRIMETHYLHEXANE	C9H20-3	1.20	0.43	0.00	0.00	
2,2,5-TRIMETHYLHEXANE	2,2,5-TRIMETHYLHEXANE	C9H20-4	0.74	0.26	0.00	0.00	
*NAPHTHALENE	NAPHTHALENE	C10H8	0.25		0.00	0.00	
C10 AROMATICS	N-BUTYLBENZENE	C10H14-1			0.00	0.00	
TERT-BUTYLBENZENE	TERT-BUTYLBENZENE	C10H14-4	0.95		0.00	0.00	
M-DIETHYLBENZENE	M-DIETHYLBENZENE	C10H14-7	0.85		0.00	0.00	
A-PINENE	A-PINENE	C10H16-2	0.12		0.00	0.00	
B-PINENE	B-PINENE	C10H16-3	0.20		0.00	0.00	
C10 OLEFINS	1-DECENE	C10H20-5			0.00	0.00	
N-DECANE	N-DECANE	C10H22-1	0.20		0.00	0.00	
ISOMERS OF DECANE	N-DECANE	C10H22-1	2.81	0.12	0.00	0.00	
1-UNDECENE	1-UNDECENE	C11H22-2	0.17		0.00	0.00	
UNDECANE	N-UNDECANE	C11H24	0.22		0.00	0.00	
			99.81	99.97	99.83	99.53	99.64



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EXECUTIVE SUMMARY

This report presents the results of a project performed by Radian Corporation to investigate the validity of assuming ideal liquid behavior (i.e., Raoult's Law) in predicting hazardous air pollutant emissions from petroleum storage tanks.

API arranged for samples of three crude oils (Mid-Continent, Alaska North Slope, and Alaska North Slope spiked with natural gas liquids) and two refined products (JP-4 aviation fuel and No. 2 fuel oil) to be shipped to Radian. Liquid and equilibrium vapor samples were analyzed for a suite of twelve selected species; liquid and vapor molecular weights were also measured.

The measured liquid composition data were used as input to a flash calculation routine in the process simulator ASPEN/SP®. In addition to Raoult's Law, the Redlich-Kwong-Soave (RKS) and Peng-Robinson (P-R) equations of state were also used to obtain predicted vapor concentrations.

In general, the vapor concentrations predicted by Raoult's Law and the two equations of state did not vary greatly among themselves. On the average, the predicted concentrations using the RKS equation of state were about 5% higher than those obtained using Raoult's Law, while the concentrations predicted by the P-R equation of state were about 18% higher than for Raoult's Law. Since these differences are within the precision and accuracy of the analytical techniques for the liquid, the data obtained in this project do not present any compelling reason to use the equations of state over Raoult's Law.

Comparisons were made of the K-values obtained using the predicted and measured vapor concentrations; the measured liquid concentrations were used in both cases. In general, the predicted and measured K-values were within the ranges expected, based on the accuracy and precision of the analytical techniques used.

Both measured and predicted K-values depend on the value of the liquid molecular weight used in the computations. The analytical techniques used (gas chromatography and gel permeation chromatography), as well as the method used to interpret the analytical data (e.g., number average versus weight average molecular weights) gave widely varying results, especially for the crude oil samples. Some of the uncertainty in the liquid molecular weight could be eliminated by performing a more complete liquid analysis. The increased analysis costs would need to be weighed against the improved confidence in the emission estimates obtained.

We recommend that the findings of this project be confirmed by conducting field measurements. Such a program would allow additional variables to be studied that might impact air toxics emissions from tanks, such as vapor and/or liquid stratification, tank type, and temperature range. In addition, it would be useful to determine the applicability of Raoult's Law to mixtures of hydrocarbons and non-hydrocarbon constituents (e.g., reformulated gasolines containing MTBE).

1.0 INTRODUCTION

1.1 Background

In 1990, Radian performed a project for API to review and assess the validity of the methodology proposed in the Midwest Research Institute report "Estimating Air Toxics Emissions from Organic Liquid Storage Tanks," EPA-450/4-88/004, October 1988. The MRI report suggested that total VOC emissions from storage tanks be estimated using the methodology presented in API publications (and their equivalents found in AP-42). To estimate emissions of specific air toxics, MRI suggested that if vapor composition data on air toxics species were not available, liquid composition data might be used to predict the vapor composition using Raoult's Law.

Under the previous project, Radian tested the validity of the Raoult's Law assumption using data for two gasolines. Vapor compositions predicted from liquid composition data using Raoult's Law as well as two equations of state (Peng-Robinson and Redlich-Kwong-Soave) were compared to the measured vapor composition data. Based on these comparisons, it appeared that fairly good estimates could be obtained using either Raoult's Law or the equations of state.

Radian recommended that additional vapor/liquid composition data for other crude oils or products be obtained to further test the validity of the Raoult's Law assumption. We suggested that one way to do this would be to obtain samples from the field and measure vapor and liquid compositions in the laboratory. API contracted with Radian in January 1991 to conduct a follow-on project to obtain such data.

1.2 Purpose of the Project

The purpose of the follow-on project was to extend the results of the previous project to include several crude oils and refined products. Samples were to be obtained from the field and the liquid and equilibrium vapor samples analyzed for selected species. The liquid composition data were to be used to predict vapor-phase concentrations of the selected species using Raoult's Law and the two equations of state used previously. Comparisons were to be made of the predicted vapor concentrations and those obtained by direct measurement.

1.3 Scope of Work

The scope of work of this project, entitled "Emissions Calculation Validation Program -- Phase II," included the following:

- Define the program by: (1) selecting the "target compounds" to be quantified, (2) determining which crude oils and refined products to be included in the project, and (3) obtaining samples for vapor and liquid analysis;
- Analyze the samples, to determine liquid and vapor molecular weights, and speciate for the target compounds of interest;
- Perform equilibrium flash calculations using the Aspen/SP® process simulator, to obtain predictions of vapor composition based on the measured liquid composition data from the analytical task; and
- Prepare a report detailing the findings and providing appropriate conclusions and recommendations.

During the project definition phase, which was performed in consultation with members of the API Evaporative Loss Measurement Committee, the following set of target compounds were selected to be speciated in the liquid and vapor samples:

- Butane,
- n-Hexane,
- Benzene,
- Cyclohexane,
- Toluene,
- Octane,
- Ethylbenzene,
- m,p-Xylenes,
- o-Xylene,
- Isopropylbenzene,
- 1,2,4-Trimethylbenzene, and
- Naphthalene.

Most of the compounds selected represent air toxics expected to be present in the crude oils and products. Butane, hexane, and octane were selected because it was felt that they might be likely to contribute significantly to the total vapor above the selected crude oils and products.

The following crude oils and products were included in the scope of this project, again in consultation with members of the API Evaporative Loss Measurement Committee:

- Mid-Continent crude oil;
- Alaska North Slope (ANS) crude oil;
- ANS crude oil spiked with natural gas liquids;
- JP-4 Aviation Fuel; and
- No. 2 Fuel Oil.

Mr. J. K. Walters took the lead, with the assistance of the API Committee members, in obtaining sample containers and shipping them to the field, contacting API member company personnel to take the samples, providing sampling instructions, and arranging for the samples to be shipped to Radian's Austin laboratories for subsequent analysis. The Mid-Continent crude sample was obtained from Texaco (Rick Barrett, Salem, Illinois), the ANS samples from Alyeska Pipeline Services Co. (Mike Kopp, Anchorage, Alaska), and the JP-4 and No. 2 Fuel Oil from Phillips' Sweeney Refinery (Bob Baird, Sweeney, Texas).

To check sample integrity, a comparison was made of the density of the materials at the time of sampling in the field, and the density as measured after the samples were received. Density measurements after receipt were to be performed by E. W. Saybolt & Co., Inc. in Houston, Texas. In addition to density, Saybolt was also requested to measure Reid Vapor Pressure; these measurements were to be compared to "typical" measured values for the crude oils and products in question.

1.4 Report Contents

Following this introductory section, the results of the analyses performed on the crude oil and product samples are presented and discussed in Section 2.0. The results of the modeling study performed to obtain predicted vapor concentrations using the measured liquid composition data are given in Section 3.0. Finally, conclusions and recommendations are presented in Section 4.0. Appendices are included that present the detailed GPC and GC/FID analytical conditions, quality assurance/quality control measures and results, and detailed tables of ASPEN/SP® modeling results.

2.0 SAMPLE ANALYSIS

Section 2.1 presents a brief discussion of the analytical instrumentation and procedures used to acquire the data. The analytical results are summarized in Section 2.2, together with observations and comments regarding these results. The quality control checks used to insure and assess data quality are provided in Appendix B.

2.1 Analytical Procedures

The parameters measured during this project were density, vapor pressure, molecular weight (vapor and liquid phase), and speciation data for selected target compounds. The preparation of samples prior to and during analysis is discussed below along with the instrumentation and methods used during the project.

2.1.1 Sample Preparation

Each of the refined products and crude oils was collected in quadruplicate by API member company personnel in 1-liter Core Labs steel sample containers and either shipped to Radian or held for pick-up by Radian personnel. Upon arrival at Radian and prior to sample analysis, the samples were stored under refrigeration at about 4°C. Two samples of each type were retained at Radian for further analysis while the remaining two samples were delivered to E.W. Saybolt & Co., Inc. for vapor pressure and density determinations; these parameters were measured to insure that sample integrity had been maintained throughout sample shipping and handling.

Sample replicates analyzed for Reid vapor pressure (Grabner) and density were chilled to 0°C during sample transfer from the sample bomb to the RVP reservoir. The samples were handled and analyzed in accordance with ASTM Method ES-15 for RVP and D-1298 for density.