

Evaluation of Fuel Tank Flammability of Low RVP Gasolines

Health and Environmental Sciences Department
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ABSTRACT

The changes in fuel properties brought on by the reformulation of gasoline to reduce VOC emissions in urban areas with severe ozone problems have raised concerns about potential impacts on the flammability of hydrocarbon vapors in closed storage vessels such as automobile fuel tanks. A desire to define the effects of reformulated gasoline (RFG) on flammability temperature limits prompted this study. Several experiments were performed to evaluate the conditions under which the vapors from reformulated gasoline (RFG) contained in automobile fuel tanks become flammable. The program was conducted with 22 test fuels that had been systematically varied with respect to Reid vapor pressure (RVP), pentane-to-butane ratio, and addition of ethanol and MTBE. In Phase I, vapor pressures were measured for each test fuel over a 15 to 130°F temperature range. In addition, the upper and lower temperature limits of flammability were measured for each fuel. Phase II involved measurements of the concentrations of hydrocarbons in the vapor phase and an assessment of stratification.

The results show that temperature limits of flammability correlate with RVP. The upper flammability temperature limits increase as RVP is reduced. The addition of either MTBE or ethanol or both to gasoline indicates a moderate increase in upper flammability limits. Gasoline blends containing ethanol, including those commingled with MTBE, elevate the upper flammability limits more substantially than do gasoline blends containing MTBE. The lower temperature limits of flammability also increase as RVP is reduced, although less markedly than the upper limits.

The flammable concentration limits of the gasolines containing ethanol are substantially greater than those containing MTBE or no oxygenates. The flammable concentration limits of gasolines containing MTBE are only slightly higher than those of the test gasolines with no oxygenates. The ratio of C₅-to-C₄ hydrocarbons in the fuel has no consistent effect on either the upper temperature limits of flammability or the upper concentration limits of flammability when comparing fuels at similar RVP levels.

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GLOSSARY OF TERMS

Lower Concentration Limit of Flammability (LCLF) - The lowest concentration of vapor in dry air which will propagate a flame away from an ignition source. (The lean flammability limit of the fuel vapor.)

Upper Concentration Limit of Flammability (UCLF) - The highest concentration of vapor in dry air which will propagate a flame away from an ignition source. (The rich flammability limit of the fuel vapor.)

Lower Temperature Limit of Flammability (LTLF) - Temperature at which the lower concentration limit of flammability (LCLF) exists in dry air under conditions of vapor-liquid equilibrium. Temperatures below the LTLF result in gasoline vapor concentrations that are too low to propagate a flame away from an ignition source.

Upper Temperature Limit of Flammability (UTLF) - Temperature at which the upper concentration limit of flammability (UCLF) exists in dry air under conditions of vapor-liquid equilibrium. Temperatures above the UTLF result in gasoline vapor concentrations that are too high to propagate a flame away from an ignition source.



EXECUTIVE SUMMARY

The changes in fuel properties brought on by the reformulation of gasoline to reduce emissions in urban areas with severe ozone problems have raised concerns about potential impacts on the flammability of hydrocarbon vapors in closed storage vessels such as automobile fuel tanks. Recent changes to gasoline which are needed to meet the federal requirements for reformulated gasoline (RFG) include the addition of ethanol and/or methyl *t*-butyl ether (MTBE), reduction in the benzene content, and lower Reid vapor pressure (RVP). The primary means for lowering RVP is to reduce the amount of butane in the gasoline. Lowering the RVP results in a decrease in the concentration of hydrocarbon vapors in the vapor space above the fuel. For gasoline, this decrease would tend to raise the upper temperature limit of flammability (UTLF). Oxygenates also could increase the upper temperature limit of flammability of fuel vapors as these compounds generally have wider flammability limits than hydrocarbons. At temperatures below the upper temperature limit of flammability, the concentration of vapors in a fuel tank can fall to the point where there is sufficient air or oxygen to sustain combustion or an explosion if an adequate ignition source is present.

In 1995, the American Petroleum Institute (API) sponsored a study to define the effects of reformulated gasoline (RFG) on flammability temperature limits. The study was conducted on 22 test fuels that had been systematically varied with respect to RVP, pentane-to-butane ratio, and concentrations of ethanol and MTBE. In Phase I, vapor pressures of each of these test fuels were measured over temperatures ranging from 15 to 130°F. Correlations were developed to predict vapor pressures as functions of temperature for the various fuels. Upper and lower temperature limits of flammability were determined and correlated with vapor pressure and differences in composition.

Phase II involved measurements of the concentrations of hydrocarbons in the vapor phase at the upper temperature limit of flammability (UTLF) of each test fuel and correlation of these results with the predicted upper concentration limits of flammability

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reported in Phase I. Phase II also entailed an assessment of stratification in an automobile fuel tank. Experiments were performed to study the interaction of temperature change, air dilution and mass diffusion rate with respect to changes in vapor-liquid equilibrium in fuel tanks.

The reader should be aware that this study is not an assessment of the "risk" of igniting vapors from low RVP and oxygenated fuels in a fuel tank. Such an assessment would have required both a detailed technical analysis of potential sources of ignition and the determination of the probabilities of igniting flammable fuel tank vapors by the various sources. That type of analysis was beyond the scope and level of resources available for this effort.

The following key findings result from the experiments conducted in this study:

- The temperature limits of flammability correlate with RVP. The upper flammability temperature limits increase as RVP is reduced. The temperature limits for non-oxygenated fuels correlate well with prior studies. The addition of either MTBE or ethanol or both to gasoline yields a moderate increase in upper flammability limits. Gasoline blends containing ethanol, including those commingled with MTBE, elevate the upper temperature limits of flammability to a greater extent than gasoline blends containing MTBE alone. The lower temperature limits of flammability also increase as RVP is reduced, although less markedly than the upper limits.
- The Clausius-Clapeyron relationship accurately defines vapor pressure as a function of the temperature and Reid vapor pressure for each of the test gasoline and gasoline/oxygenate blends.
- A generalized expression for the dependence of vapor pressure on absolute temperature and RVP can be established for each fuel group, i.e., neat gasoline, gasoline/MTBE blends, etc.
- The upper concentration limits of flammability (UCLF) of the gasolines containing ethanol are markedly greater than those containing MTBE or no oxygenates. The UCLF of gasolines containing MTBE are only slightly higher than the limits of the test gasolines containing no oxygenates.

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- The ratio of C_5 -to- C_4 hydrocarbons in the fuel has no consistent effect on the measured values of either the upper temperature limits of flammability or the upper concentration limits of flammability when comparing fuels at similar RVP levels.
- Stratification of vapors in fuel tanks results from changes in temperature which cause air to enter (or be ingested by) the tank. Deviations of vapor concentrations from equilibrium conditions in a fuel tank are explainable in terms of air ingestion resulting from temperature change and mass transport effects on the re-establishment of equilibrium. At constant temperature, up to 4 hours are required to reach vapor-liquid equilibrium in a closed storage vessel.
- A decrease in temperature causes air to enter and dilute the fuel vapors in a fuel tank. The effect of air dilution on fuel tank vapor concentration is somewhat offset by lags between changes in ambient temperature and fuel temperature which can be as much as 3 hours. When the ambient temperature falls, the reduction in fuel temperature lags behind and this causes the concentration of vapors in the tank to remain higher than the equilibrium concentration for the ambient temperature.
- The air dilution and molecular diffusion associated with a 24-hour diurnal cycle over an 84 to 60 °F ambient temperature range has a relatively small effect on the departure of vapor concentrations in a fuel tank from equilibrium conditions. The vapor concentration does not fall more than 20% below equilibrium levels. The effects of these two phenomena (air dilution and molecular diffusion) on the dynamics of vapor-liquid equilibrium concentrations in a fuel tank are only important (with respect to reaching the UCLF) when there are rapid changes in ambient temperature.

Section 1

INTRODUCTION

Most accidents involving fire are caused by fuel tank rupture. Spilled gasoline is the worst of fire hazards because its vapors can be ignited and can quickly envelop the vehicle. Other fire hazards involve fuel leaks in the engine compartment where the hot exhaust manifold and corona discharge around ignition wires are potential ignition sources. On the other hand, very few, if any, fire-related accidents in automobiles have been attributed to explosions within the fuel tank. Therefore, fuel tank flammability is a safety concern that has not been extensively studied.

One reason that there has been limited investigation of fuel tank vapor flammability is that the vapors in a fuel tank are often not flammable. At temperatures above a certain level, the concentration of gasoline vapors relative to air in the vapor space of an automotive fuel tank is well in excess of the point where the mixture would become flammable (i.e., the rich or upper flammability limit) if exposed to an ignition source.⁽¹⁾ Conversely, when the fuel temperature falls below a certain level, the concentration of air relative to fuel vapors in the tank prevents ignition from occurring (i.e., the lean or lower flammability limit). Consequently, between these two temperature limits, the vapors are flammable and could be ignited if subjected to a sufficiently intense ignition source. Temperatures that define the flammable range of the fuel vapor are termed the upper and lower temperature limits of flammability. Temperature limits of flammability are affected by Reid vapor pressure (RVP) and fuel composition.

Congress, through the Clean Air Act Amendments of 1990, required that a cleaner burning gasoline be used in the nine cities in the United States with the worst urban ozone levels in 1995. Specifications were set to define a "Reformulated Gasoline" (RFG) to reduce the exhaust and evaporative emissions of ozone-forming compounds and air toxics, such as benzene. Table 1-1 compares the properties of conventional gasoline versus RFG produced to meet EPA's performance requirements using the EPA "Simple

Model." Most of the changes to meet the specifications under the "Simple Model" are accomplished by adding ethanol and/or methyl *t*-butyl ether (MTBE) and by lowering the butane content. The change with the greatest impact on fuel tank flammability, however, is reduced RVP. Reduced vapor pressure decreases evaporative emissions but hinders cold startability and elevates the upper temperature limit of flammability.

Table 1-1. Fuel Parameters for Conventional Gasoline and "Simple Model" RFG			
Fuel Property	Conventional Gasoline		Simple Model RFG
	Average*	Range†	
RVP,‡ psia	8.7(S) 11.5(W)	6.9-10.1(S) 9.9-15.1(W)	7.2/8.1(S) 11.5(W)
T50, °F	207	178-251(S) 166-239(W)	n/a
T90, °F	332	307-369(S) 286-357(W)	≤ 1990 Refinery Baseline Avg
Aromatics, vol%	28.6	6.1-52.2(S) 6.6-47.2(W)	Controlled as Necessary to Meet the Toxics Emissions Performance Std.
Olefins, vol%	10.8	0.4-26.0(S) 0.4-29.9(W)	≤ 1990 Refinery Baseline Avg
Benzene, vol%	1.60	0.1-3.89(S) 0.1-5.18(W)	≤0.95 Avg (1.3 max)
Sulfur, ppm	338	10-1100(S) 10-1170(W)	≤ 1990 Refinery Baseline Avg
Oxygen from Oxygenates, Wt %	---	0.04-2.4(S) 0.04-2.5(W)	1.5 Min >2.1 Avg 2.7(S)/3.5(W) Max

*As defined in the Clean Air Act

†1990 Summer and Winter MVMA surveys (gasohol excluded)

‡Winter (W) higher than Summer (S) to maintain vehicle performance

The primary means for lowering RVP is to reduce the amount of butane in the gasoline. Decreasing the RVP results in an increase in the air-fuel ratio and this tends to raise the upper temperature limit of flammability. Oxygenates also could increase the upper temperature limit of flammability as they generally have wider flammability limits than hydrocarbons. The introduction of RFG, therefore, has the potential of affecting flammability limits, and increases in the upper temperature limit of flammability raise the potential risk of a fuel tank explosion. A desire by the American Petroleum Institute (API) to define the effects of RFG on flammability temperature limits prompted this study.

In the present study, Southwest Research Institute (SwRI) was contracted by API to evaluate the effects of RVP and fuel composition on the flammability of RFG vapors in fuel tanks. The study was conducted on 22 test fuels that had been systematically varied with respect to RVP, pentane-to-butane ratio, and concentrations of ethanol and MTBE. In Phase I, vapor pressures of each of these test fuels were measured over temperatures ranging from 15 to 130°F. Correlations were developed to calculate vapor pressures as functions of temperature for the various fuels. Upper and lower temperature limits of flammability were determined and correlated with vapor pressure and differences in composition.

Phase II involved measurements of the concentrations of hydrocarbons in the vapor phase at the upper temperature limit of flammability (UTLF) of each test fuel and correlation of these results with the UTLF measurements reported in Phase I. Phase II also entailed an assessment of stratification in an automobile fuel tank. Experiments were performed to determine the effects of temperature change and mass diffusion on the time needed to attain a fuel vapor-liquid equilibrium in fuel tanks.

The term "RVP" is used in this document for convenience at times to truly mean Reid vapor pressure and at other times to mean "Dry Vapor Pressure Equivalent" (DVPE). The DVPE values were obtained using a Grabner vapor pressure meter and employing

the American Society for Testing and Materials (ASTM) test method D 5191.⁽¹³⁾ This procedure reports a correlated DVPE which is equivalent to that provided from ASTM D 4953⁽¹³⁾, the standard test method for measuring the vapor pressure of gasoline and gasoline-oxygenate blends. As ASTM D 4953 is, itself, a modification of the traditional ASTM D 323⁽¹⁴⁾ test method for measuring Reid vapor pressure, DVPE can be considered a surrogate for RVP.

Section 2

TEST FUELS

FUELS PROCUREMENT AND FORMULATION

Three reformulated baseline gasolines (FL2221, FL2222, and FL2223) were procured from Phillips Petroleum Company (PPC). The PPC fuels met the basic specifications of Phase I reformulated gasoline described in Table 1-1. However, the gas chromatographic analysis revealed higher than desired levels of C_4 hydrocarbons, cyclopentane, cyclohexane, and n-heptane. Since the hydrocarbon composition of the PPC fuels was somewhat atypical of reformulated gasolines, the fuel matrix was complemented with two additional baseline fuels (FL2407 and FL2408) that were formulated to provide vapor pressures similar to the PPC fuels FL2223 and FL2221 but with a more typical distribution of species and minimal amounts of butane. One of these new fuels (FL2408) was further modified late in the program by adding C_5/C_6 isomerate to create two additional gasolines (FL2409 and FL2410) that served to extend the RVP range of the baseline gasoline fuel set.

The new fuels were blended according to the formulations shown in Table 2-1. All of the fuel components were typical gasoline blendstocks except for the de-butanized alkylate and the hydrotreated Fluidized Catalytic Cracked (FCC) heavy gasoline. The reformat (95 RON platformate) was obtained from PPC, while the "FCC Heavy" and "FCC Light Naphtha" gasolines were obtained through API. The hydrotreated FCC heavy gasoline was made by hydrotreating the gasoline in the SwRI Alternative Fuels Center. The alkylate was provided by Coastal States Petroleum Company in Corpus Christi, Texas, and was de-butanized because it contained about 5 percent butane in its original state. The de-butanization was performed by cooling the alkylate to 45°F and purging with nitrogen. Lowering the temperature favored the relative volatilization of the lighter hydrocarbons. The C_5/C_6 isomerate was procured from Southwestern Refining Company.

Table 2-1. Composition of Baseline Gasolines Prepared at SwRI

Fuel Component	RVP, psia	Specific Gravity	Baseline Gasoline ID (RVP, psia)			
			FL2407 (5.37)	FL2408 (7.29)	FL2409 (7.89)	FL2410 (8.94)
			wt% (vol%)	wt% (vol%)	wt% (vol%)	wt% (vol%)
Reformate	1.8	0.7980	25.00 (26.68)	24.00 (25.94)	22.82 (20.80)	20.42 (18.33)
FCC Heavy	1.7	0.7775	6.00 (6.24)	5.00 (5.27)	4.76 (4.45)	4.26 (3.93)
SwRI FCC Heavy Hydrotreated	1.6	0.8163	16.00 (17.47)	15.00 (16.59)	14.27 (12.71)	12.77 (11.21)
De-Butanized Alkylate	3.1	0.7062	30.00 (28.33)	22.00 (21.05)	20.92 (21.54)	18.72 (18.99)
FCC Light Naphtha	9.2	0.7119	17.00 (16.18)	18.00 (17.36)	17.11 (17.49)	15.32 (15.42)
C ₅ /C ₆ Isomerate	16.7	0.6360	6.00 (5.10)	16.00 (13.79)	20.12 (23.01)	28.51 (32.12)

FUEL ANALYSIS

Fuel speciation was performed with a Hewlett-Packard model 5890 gas chromatograph equipped with a 105-m capillary column and a flame ionization detector. Data acquisition was performed with Chrom Perfect software designed specifically for speciation and PIANO analysis of complex hydrocarbon mixtures. The 105-m capillary column was obtained from Restek Corporation, and calibration standards consisting of 167 hydrocarbons were obtained from Supelco, Inc. Chromatograms on several off-the-shelf compounds were run and added to the hydrocarbon data base. Fluorescence Indicator Analysis (FIA) was used to measure the volume fractions of saturates, olefins, and aromatics in the baseline gasolines. Table 2-2 presents fuel properties and composition, while Table 2-3 shows the ASTM D 86 boiling point distributions of the baseline gasolines. Fuels FL2409 and FL2410 are absent from Tables 2-2 and 2-3. As noted

previously, these two fuels were included late in the program and consequently were not measured for most of the properties shown in Tables 2-2 and 2-3.

Table 2-2. Baseline Gasoline Properties and Compositions					
Baseline Gasoline (Source)	FL2223 (PPC)	FL2222 (PPC)	FL2221 (PPC)	FL2407 (SwRI)	FL2408 (SwRI)
Fuel Property					
Specific Gravity	0.7523	0.7500	0.7460	0.7447	0.7339
Dry Vapor Pressure Equivalent (DVPE), psia	5.40	6.35	7.15	5.37	7.29
C ₄ Hydrocarbons, wt%	1.58	2.43	3.08	0.38	0.52
C ₅ Hydrocarbons, wt%	8.99	8.28	9.82	11.09	19.13
C ₆ Hydrocarbons, wt%	22.20	20.66	21.79	8.61	13.35
C ₇ Hydrocarbons, wt%	20.69	19.59	19.90	14.52	17.73
C ₈ Hydrocarbons, wt%	29.15	26.62	26.09	31.25	29.83
C ₉₊ Hydrocarbons, wt%	17.39	22.42	19.32	34.15	19.44
Benzene, wt%	1.13	1.05	1.11	0.82	0.95
Toluene, wt%	7.48	7.03	7.17	7.78	7.92
Butane, wt%	1.58	2.42	3.08	0.38	0.45
n-Pentane, wt%	0.96	0.90	1.06	2.08	5.30
iso-Pentane, wt%	2.63	2.42	3.15	6.04	9.05
Cyclopentane, wt%	3.42	3.15	3.50	0.27	0.69
Cyclohexane, wt%	8.77	8.11	8.47	0.10	0.10
iso-Octane, wt%	9.97	7.34	7.54	10.39	9.65
n-Heptane, wt%	4.15	3.87	3.97	0.80	0.88
Saturates, vol%*	70.3	67.1	69.4	68.8	70.1
Aromatics, vol%*	22.4	24.7	23.3	24.7	22.9
Olefins, vol%*	7.3	8.2	7.3	6.3	7.0

* Analysis by FIA method

Table 2-3. ASTM D 86 Boiling Point Distributions of Baseline Gasolines, °F					
Base Fuel	FL2223	FL2222	FL2221	FL2407	FL2408
% Evaporated					
IBP*	109	104	96	103	95
5	145	130	125	132	115
10	159	149	144	149	129
20	177	173	167	175	146
30	190	189	185	197	165
40	203	204	199	215	189
50	216	217	214	231	214
60	228	234	229	244	235
70	250	253	250	263	254
80	281	279	278	293	282
90	330	321	325	334	326
95	370	366	351	363	359
EP†	409	409	407	415	415

* IBP = Initial boiling point

† EP = End point

Fuels FL2223 and FL2407 had DVPEs of ≈ 5.3 psia, and fuels FL2221 and FL2408 had DVPEs of ≈ 7.2 psia. However, the light-end compositions of both pairs of test gasolines were very different. These differences between the fuels of similar RVP are reflected both in the hydrocarbon analyses and in the boiling point distributions. By design, the ratio of C_5 -to- C_4 hydrocarbons was much higher in the SwRI fuels (FL2407 and FL2408) than in the PPC fuels (FL2221, FL2222 and FL2223). Because of these differences in C_5 -to- C_4 ratios, iso-pentane should be the predominate species in the vapor phase of fuels FL2407, FL2408, FL2409, and FL2410, while butane should dominate the vapor phase of fuels FL2221, FL2222, and FL2223.

It can be seen in Table 2-2 that the PPC fuel set contains substantially more C_6 and C_7 hydrocarbons than does the SwRI fuel set, particularly with the 5.4 psi RVP fuels. The high concentrations of $C_{6,7}$ hydrocarbons (and lower concentrations of C_5 hydrocarbons) in the PPC fuels compensate for the abnormally high level of butane in these gasolines.

FUEL MATRIX

Table 2-4 describes the 7 baseline gasoline and 15 oxygenated gasoline test fuels examined in the study. The 15 oxygenated gasoline blends were made by splash blending ethanol, MTBE, and an ethanol/MTBE mix into each of 5 of the baseline gasolines (FL2221, FL2222, FL2223, FL2407 and FL2408). Five fuels were produced by splash blending 10 vol% ethanol into each of these 5 baseline gasolines. (These fuels are labeled with the code "FLnnnnA", where the "A" indicates ethanol and the "nnnn" refers to the numerical designation of the corresponding base fuel.) Five more fuels were produced by splash blending 15 vol% MTBE into each of the 5 aforementioned baseline gasolines. (The MTBE fuels are identified with the code "B" using the convention described above.) The last 5 fuels were made by commingling equal portions of the 10 percent ethanol and 15 percent MTBE blends. (The commingled oxygenated fuels are coded with the letter "C.") The other 2 baseline gasolines (FL2409 and FL2410) were not blended with any oxygenate. These 2 fuels were included only for the purpose of extending the vapor pressure range of the baseline gasolines.

Table 2-4. Test Fuel Descriptions

Code Name	Description	Blending Site	DVPE, psia
FL2221	Baseline Gasoline	PPC	7.15
FL2221A	FL2221 + 10 vol% Ethanol	SwRI	8.10
FL2221B	FL2221 + 15 vol% MTBE	SwRI	7.51
FL2221C	50 vol% FL2221A + 50 vol% FL2221B	SwRI	8.13
FL2222	Baseline Gasoline	PPC	6.35
FL2222A	FL2222 + 10 vol% Ethanol	SwRI	7.44
FL2222B	FL2222 + 15 vol% MTBE	SwRI	6.94
FL2222C	50 vol% FL2222A + 50 vol% FL2222B	SwRI	7.51
FL2223	Baseline Gasoline	PPC	5.40
FL2223A	FL2223 + 10 vol% Ethanol	SwRI	6.58
FL2223B	FL2223 + 15 vol% MTBE	SwRI	6.19
FL2223C	50 vol% FL2223A + 50 vol% FL2223B	SwRI	6.68
FL2407	Baseline Gasoline	SwRI	5.37
FL2407A	FL2407 + 10 vol% Ethanol	SwRI	6.55
FL2407B	FL2407 + 15 vol% MTBE	SwRI	6.07
FL2407C	50 vol% FL2407A + 50 vol% FL2407B	SwRI	6.72
FL2408	Baseline Gasoline	SwRI	7.29
FL2408A	FL2408 + 10 vol% Ethanol	SwRI	8.33
FL2408B	FL2408 + 15 vol% MTBE	SwRI	7.71
FL2408C	50 vol% FL2408A + 50 vol% FL2408B	SwRI	8.24
FL2409	Baseline Gasoline	SwRI	7.89
FL2410	Baseline Gasoline	SwRI	8.94

Section 3

PHASE I STUDY

This section presents the vapor pressure measurements that were performed during Phase I of the study. The procedures and results of the experiment to quantify temperature limits of flammability also are detailed.

VAPOR PRESSURE MEASUREMENTS

Apparatus and Procedure

Vapor pressures were measured with a Grabner model CCA-VPS and a Grabner model CCA-VP equipped with Peltier cooler. The model CCA-VPS was used to measure vapor pressures in the 70 to 130°F range, while the model CCA-VP was used to measure vapor pressures in the 15 to 70°F range. For the latter, a separate fluid cooling apparatus was used to assist the Peltier cooler in reaching temperatures below 30°F. The instruments were calibrated with 2,2-dimethyl butane and n-pentane standards. Also, data on neat ethanol were compared with literature data.⁽²⁾ Vapor pressures of neat ethanol, neat MTBE, and the 22 test fuels were measured at 14 temperatures in the 15 to 130°F range. Several measurements were made at low temperatures (15 to 30°F) or in the region of the upper temperature limits of flammability of the test fuels.

Results

The vapor pressure data are given in Tables A-1 through A-4 in Appendix A. Figure 3-1 shows Clausius-Clapeyron plots⁽³⁾ of the neat ethanol and neat MTBE data. The measured vapor pressures for ethanol are in good agreement with the literature data⁽²⁾ in the figure. The slope of the curve for ethanol is steeper than that for MTBE because ethanol has a significantly higher heat of vaporization. Figures A-1 through A-4 in Appendix A show Clausius-Clapeyron plots of the vapor pressures of the 22 gasoline and gasoline/oxygenate test fuels. It can be seen in Figure A-1 and Table A-1 that the baseline gasolines with similar RVPs, i.e., fuels FL2223 and FL2407 and fuels FL2221 and FL2408, have similar vapor pressures throughout the temperature range of 15 to

130°F. The same behavior is also noted for the oxygenated gasoline blends containing ethanol, MTBE, and a mixture of ethanol/MTBE, i.e., blends with similar RVPs have similar vapor pressures throughout the temperature range.

The fuel blends containing ethanol and MTBE have higher vapor pressures than the baseline gasolines. MTBE is expected to increase the RVP because its vapor pressure is higher than the vapor pressures of the gasolines that were blended with MTBE. The addition of ethanol to the base gasoline caused the Reid vapor pressures of the resulting blends to increase by 1.0 to 1.2 psi even though the RVP of ethanol is substantially less than the RVPs of the base gasolines. The RVP of neat ethanol is lower than its molecular weight would suggest because of hydrogen bonding between the molecules. When ethanol is dissolved in gasoline, the hydrogen bonding is disrupted and its effective vapor pressure is increased and is more representative of its low molecular weight.

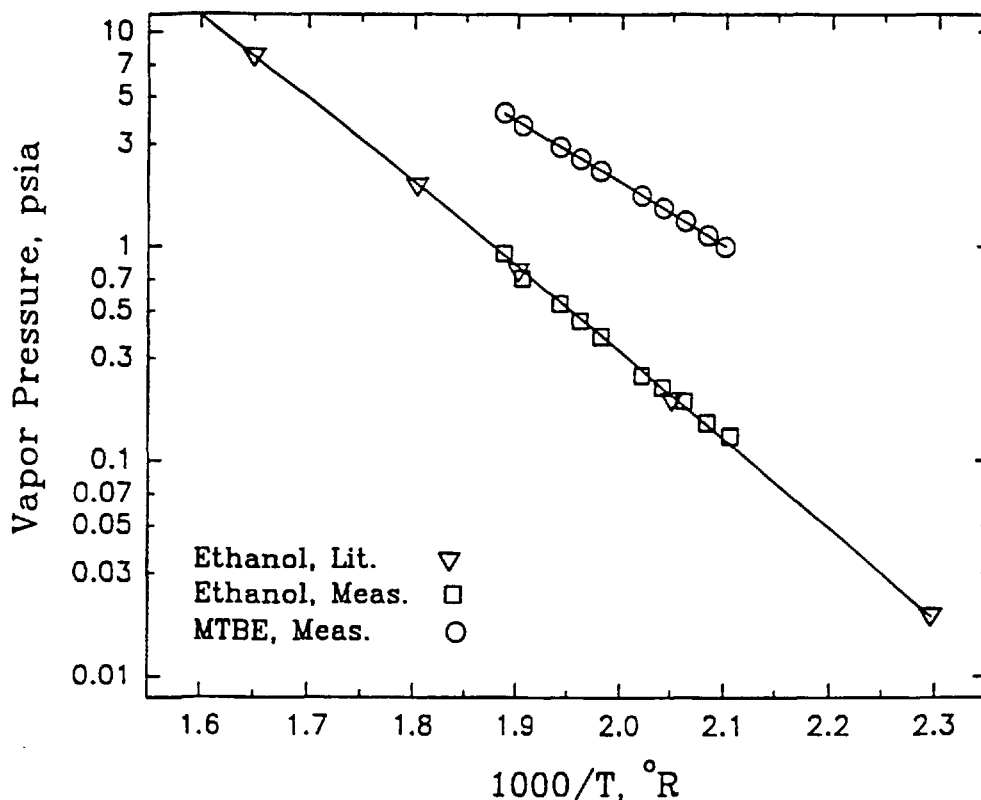


Figure 3-1. Clausius-Clapeyron plots for ethanol and MTBE showing the effect of temperature on vapor pressure

The vapor pressure data for each test fuel were correlated according to the expression

$$\text{Log}_{10}(P_{\text{vap}}) = A + \frac{B}{T} + \frac{C}{T^2} \quad (\text{Eq. 1})$$

where P_{vap} is the vapor pressure in psia; T is the absolute temperature in °R; and A , B , and C are correlation coefficients. Table 3-1 gives the correlation coefficients determined for each test fuel, including neat ethanol and MTBE.

Table 3-1. Coefficients for the Expression $\text{Log}_{10}(P_{\text{vap}}) = A + B/T + C/T^2$ Where P_{vap} is in psia and T is in °R			
Fuel Name	A	B	C
FL2221	3.587	-631.1	-505,880.3
FL2222	4.017	-1,104.4	-392,592.2
FL2223	5.413	-2,671.0	-25,410.7
FL2407	4.590	-1,790.9	-208,978.8
FL2408	3.217	-167.7	-644,537.1
FL2409	3.982	-1,015.9	-396,474.8
FL2410	4.182	-1,200.4	-337,870.2
FL2221A	4.451	-1,273.3	-398,073.7
FL2222A	4.632	-1,462.9	-360,397.4
FL2223A	4.602	-1,452.3	-372,749.4
FL2407A	5.545	-2,542.1	-57,570.1
FL2408A	5.124	-2,049.1	-168,498.8
FL2221B	2.936	184.0	-750,699.9
FL2222B	2.659	509.8	-857,787.1
FL2223B	2.367	815.8	-952,611.6
FL2407B	3.781	-799.3	-494,002.2
FL2408B	2.521	665.4	-884,767.6
FL2221C	4.252	-1,090.5	-437,482.8
FL2222C	4.129	-950.6	-488,333.1
FL2223C	4.748	-1,644.1	-309,436.0
FL2407C	5.134	-2,124.8	-159,498.2
FL2408C	4.793	-1,723.1	-248,833.3
MTBE	3.303	-106.6	-697,785.0
Ethanol	6.294	-2,745.6	-326,283.0

Because all the gasoline test fuels exhibited similar vapor pressure behavior (see Figures A-1 through A-4), it was feasible to create a generalized expression for the dependence of vapor pressure on absolute temperature and RVP. A nonlinear regression analysis of the data in Tables A-1 through A-4 was correlated according to the expression

$$P = RVP \exp\left(a + \frac{b}{T} + \frac{c}{T^2}\right) \quad (\text{Eq. 2})$$

where P is the vapor pressure in psia; RVP is the Reid vapor pressure in psia; T is the absolute temperature in °R; and a , b , and c are constants.

Equations 1 and 2 are based on the Clausius-Clapeyron equation which may be expressed as

$$\ln(P_{vap}) = \frac{\Delta H_{vap}}{RT} + C \quad (\text{Eq. 3})$$

where P_{vap} is the vapor pressure in psia; ΔH_{vap} is the heat of vaporization; R is the ideal gas constant; T is the absolute temperature in °R; and C is a constant. Equation 3 indicates that $\ln(P_{vap})$ is inversely proportional to the absolute temperature. This relationship would hold completely true if the heat of vaporization were constant. In fact, there is a slight variation of ΔH_{vap} with temperature, which is the reason for the C/T^2 term in Equation 1.

The correlation was performed on all of the test fuels as a group and subsequently on each of the four fuel classes, i.e., base fuels, ethanol blends, MTBE blends and ethanol/MTBE commingled blends. Table 3-2 gives values of the empirical constants a , b , and c for each of the fuel groups.

Table 3-2. Correlation Coefficients for the Expression $P = RVP \exp(a + b/T + c/T^2)$, Where P is in psia, RVP is Reid Vapor Pressure in psia, and T is in °R

Fuel Group	Data	a	b	c
All 22 Test Fuels	296	6.540	-1419.8	-1.257×10^6
Base Fuels	101	6.229	-1384.7	-1.178×10^6
10% Ethanol Blends	65	9.044	-3877.3	-6.629×10^5
15% MTBE Blends	65	3.754	1578.0	-2.063×10^6
Ethanol/MTBE Commingled Blends	65	8.490	-3352.3	-7.837×10^5

Figure 3-2 shows excellent agreement between the vapor pressures predicted using the overall correlation and all of the measured values for the 22 gasoline test fuels that had

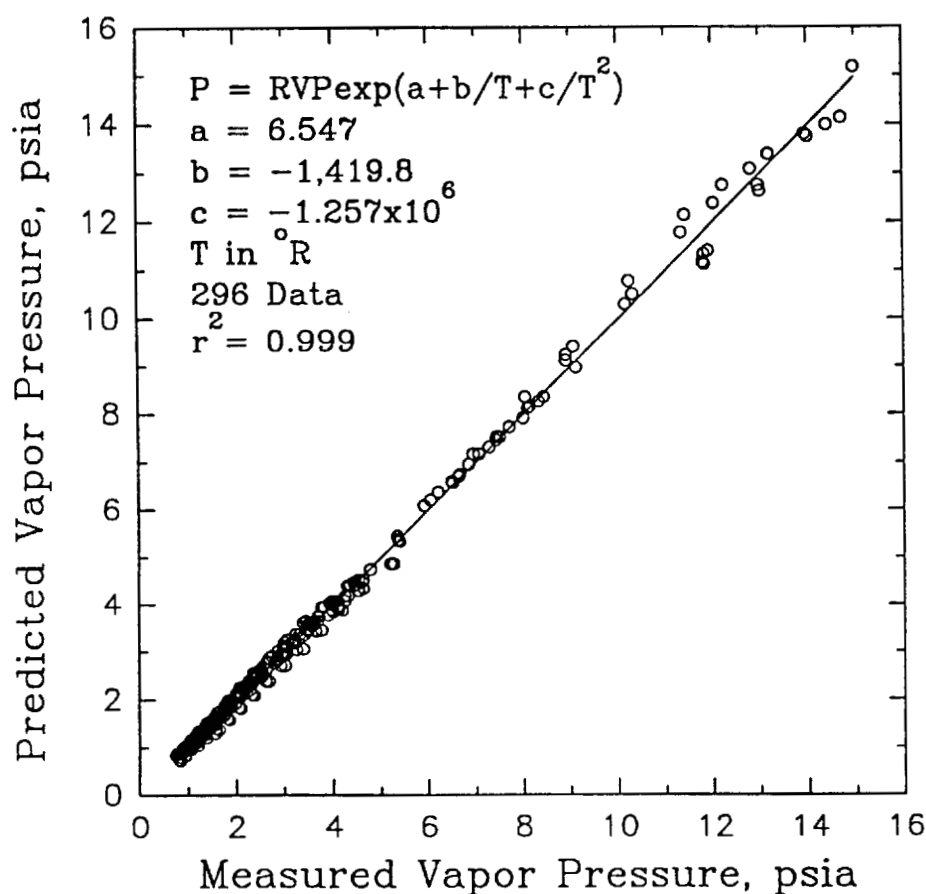


Figure 3-2. Comparison of vapor pressures predicted by Eq. 2 with measured values

been determined over the range of 15°F to 130°F. The accuracy of the correlation is exhibited in Appendix B where the numerical values of the measured and predicted vapor pressures are compared in terms of residual differences between measured and predicted. While the correlation based on all of the test fuels gave very small residuals, the residuals obtained from correlations of the individual fuel groups were even smaller. The results of the correlations shown in Table 3-2 indicate that there are slight differences in heat of vaporization among the fuel groups. The fuel groups containing ethanol had higher values of the constant b , indicating that their heats of vaporization were higher than those of the other fuel groups. However, the absolute differences in predicted vapor pressures of baseline gasolines and gasolines containing ethanol of the same RVP were less than 0.2 psia.

TEMPERATURE LIMITS OF FLAMMABILITY

Apparatus

The apparatus used in this study was similar to that used by Fanick *et al.*⁽⁴⁾ and Lawson *et al.*⁽⁵⁾ to measure flammability limits of fuel vapors. The combustion vessel shown in Figure 3-3 was a 500-mL three-neck round bottom pyrex flask. The flask dimensions were sufficient to preclude wall quenching effects on the flammability limits.^(6, 7) The electrodes for ignition and the thermocouples for measuring fuel temperature were mounted in rubber stoppers that were placed in ports of the round bottom flask. The ignitor electrodes consisted of two 10-cm lengths of 14-gauge copper wire mounted parallel in the stopper 12.7 mm apart. The copper electrodes were sharpened to a point and bent at the ends to form a 2.5-mm spark-gap at the center of the flask. The electrodes were insulated with a polyethylene sheath up to where they were bent to form the spark-gap. An automotive spark coil capable of producing a continuous 400-Hz oscillating arc discharge was used to ignite the fuel vapors. Each ignition pulse was about 70 mJ, so at a rate of 400 Hz, the source delivered ≈ 280 mJ in 0.01 seconds.^a

^a Typically, ignition coils for gasoline engines store from 60 to 120 mJ.⁽⁸⁾ This energy is delivered each time the spark plug fires.

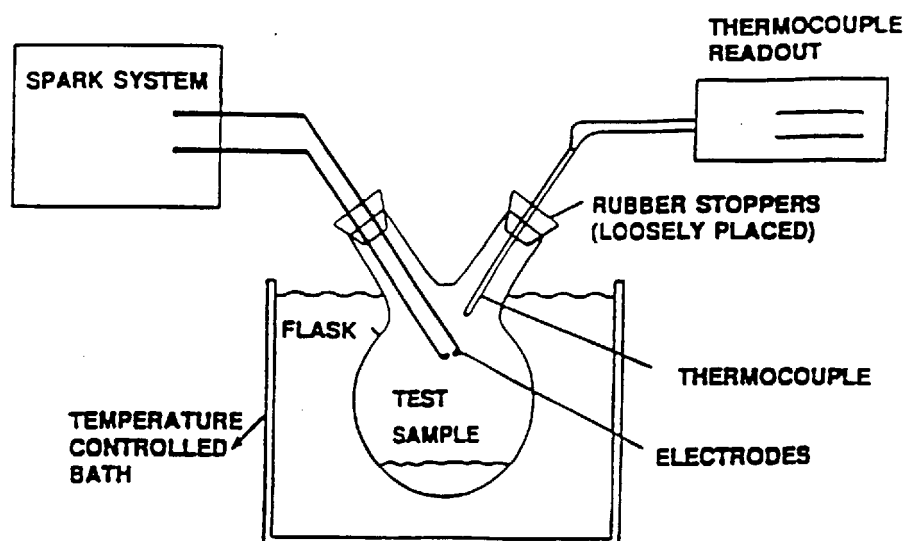


Figure 3-3. Temperature limit of flammability test apparatus

The source was left on for at least 2 seconds in each ignition test.

Aside from an open flame, an electric spark is the most effective means of ignition. A spark energy of approximately 0.2 mJ is sufficient to ignite a stoichiometric hydrocarbon-air mixture. Rich and lean mixtures require over 3 mJ.⁽⁸⁾ Therefore, a continuously firing automotive spark coil ignitor, such as that used in the present study, would be considered an overwhelming ignition source.

Procedure

The combustion vessel was filled with 25 mL of test fuel. It was agitated in order to wet the walls of the flask so the fuel would evaporate and mix with the air. The flask was immersed in a constant temperature isopropanol/water bath controlled to within 0.5°C. It required about 30 minutes for the liquid fuel and bath temperatures to equilibrate. An attempt was made to ignite the fuel-air mixture about 20 minutes after the liquid fuel and

bath temperatures equilibrated. The temperature limits of flammability were determined by a trial and error process.

At the start of testing, a target bath temperature was chosen. If ignition occurred at the chosen temperature, it would be characterized as weak, medium, or strong, depending on the aural intensity of the explosion. If the explosion was weak, the conditions were very close to the temperature limit of flammability. Therefore, in the next test the bath temperature would be raised just a few degrees. If no ignition occurred, the temperature limit was within a few degrees of the bath temperature in the last test. Once the temperature limit of flammability was bracketed to within a few degrees, tests were performed in 1°C increments to achieve accuracy to within 1°C.^b

Results

The temperature limits of flammability were derived by interpolation of the test data given in Table C-1 of Appendix C. The test results and interpolations are accurate to within $\approx 2^{\circ}\text{F}$. Table 3-3 gives temperature limits of flammability in units of $^{\circ}\text{F}$ and corresponding vapor phase concentration limits for each of the test fuels. The concentration limits in Table 3-3 were calculated for each fuel using Eq. 1 and the constants A , B , and C in Table 3-1. The upper and lower concentration limits calculated in Table 3-3 are assumed to be equivalent to the respective upper and lower flammability limits that are normally reported in the literature.

The literature values for the upper and lower flammability limits of ethanol are 18.95 and 3.28 mole percent, respectively.⁽²⁾ Table 3-3 shows upper and lower flammability limits of ethanol observed in this experiment as 12.4 and 3.64 mole percent (mole %), respectively. The lean flammability limits agree with each other reasonably well, but the

^b Hereafter, the data on temperature limits of flammability will be reported and discussed in terms of degrees Fahrenheit in order to facilitate comparisons with other studies.

Table 3-3. Limits of Flammability					
Fuel Name	RVP, psia	Temperature Limits		Concentration Limits*	
		Upper, °F	Lower, °F	Upper Mole %	Lower Mole %
Ethanol	2.41	91.4	53.6	12.40	3.64
MTBE	8.34	18.5	-14.8	7.48	2.42
Cyclohexane	3.36	49.1	5.7	6.02†	1.46†
FL2221	7.15	15.8	-41.8	7.37	1.06
FL2222	6.35	17.6	-31.0	6.68	1.41
FL2223	5.40	19.4	-23.8	6.22	1.84
FL2407	5.37	19.4	-25.6	6.12	1.59
FL2408	7.29	12.2	-34.6	6.50	1.27
FL2409	7.89	8.8	N‡	7.11	N
FL2410	8.94	2.3	N	7.02	N
FL2221A	8.10	12.2	-32.8	6.47	1.35
FL2222A	7.44	14.0	-38.2	6.07	0.95
FL2223A	6.58	21.2	-22.0	6.54	1.53
FL2407A	6.55	23.0	-25.6	7.54	1.69
FL2408A	8.33	12.2	-29.2	7.43	2.00
FL2221B	7.51	14.0	-32.8	6.67	1.24
FL2222B	6.94	15.8	-32.8	6.07	0.99
FL2223B	6.19	19.4	-22.0	5.83	1.28
FL2407B	6.07	24.8	-31.0	7.45	1.19
FL2408B	7.71	10.4	-31.0	6.01	1.28
FL2221C	8.13	6.8	-31.0	5.62	1.50
FL2222C	7.51	17.6	-29.2	6.91	1.36
FL2223C	6.68	21.2	-25.6	6.86	1.46
FL2407C	6.72	23.0	-25.6	7.81	1.73
FL2408C	8.24	10.4	-31.0	7.03	1.84

* Concentration limits calculated using vapor pressure correlations in Table 3-1.

† Concentration limits calculated using literature vapor pressure data.⁽²⁾

‡ No data

rich limit cited in the literature⁽²⁾ is 53 percent too high. Most of the flammability limits in the literature were determined at the Bureau of Mines by evidence of visible flame propagation when mixtures were ignited in glass tubes.^(6, 7, 10) Cool flame chemiluminescence is sometimes mistaken for ignition. Chemiluminescence has the

appearance of flame propagation, but it occurs without any measurable rise in pressure or temperature. Cool flames occur predominantly in fuel rich mixtures, so they often complicate the definition of the upper flammability limit.

More recent work in a constant volume combustion bomb⁽¹¹⁾ showed that the upper flammability limits of the low molecular weight alcohols are substantially lower than accepted values. This was because ignition was detected by pressure rise instead of visible flame radiation. The upper flammability limit determined for ethanol by the combustion bomb method was 14.3 mole percent, which agrees more closely with the value of 12.4 mole percent in Table 3-3.

The flammability limits of MTBE are not well documented, but when compared with butane and pentane (see Appendix D), the values in Table 3-3 seem reasonable. The upper and lower flammability limits of cyclohexane (7.75 and 1.26 mole percent,⁽²⁾ respectively) agree reasonably well with the concentration limits in Table 3-3. In general, the concentration limits in Table 3-3 are narrower than the flammability limits determined at the Bureau of Mines.^(6, 7, 10)

As mentioned above, this difference most probably results from differences between the methods used to measure flammability limits, but it may also have something to do with temperature. Most flammability limits available in the literature were measured at temperatures greater than ambient. The concentration limits in Table 3-3 were determined at temperatures well below ambient. Since flammability limits widen with increased temperature, they are expected to be narrower at lower temperatures. Temperature may play a role in explaining why the upper concentration limits of ethanol, cyclohexane, and the test fuels in Table 3-3 are slightly lower than the literature values.

In Table 3-3, the upper concentration limits of the 22 test baseline gasolines and gasoline/oxygenate blends range from 5.62 to 7.81 mole percent, and lower limits range from 0.95 to 2.00 mole percent. The upper concentration limits are similar to those

determined by Marshall and Schoonveld⁽¹²⁾ for gasolines of varying RVP. Marshall and Schoonveld sampled the vapor space in a fuel tank by pumping the gasoline-air mixture into Tedlar bags. An ignition device was used to ignite the mixture in the Tedlar bags. The mixtures seldom ignited when the vapor concentration exceeded 8 mole percent and almost always ignited when the vapor concentration was less than 6 mole percent.

Literature values for flammability limits of several hydrocarbons are given in Appendix D. Literature values in parentheses in Table D-1 seem more realistic because they were determined from evidence of pressure rise in a constant volume combustion apparatus instead of from flame luminescence. Without knowledge of the exact composition of the test fuel vapors, the upper concentration limits in Table 3-3 appear to be slightly lower than the C₄ to C₈ hydrocarbons in Appendix D. However, the comparison would probably be more favorable if it were made with literature values measured at the appropriate temperature and by evidence of pressure rise rather than flame luminescence.

Figure 3-4 shows the relationship between the temperature limits of flammability and RVP for all fuels tested. Fuels with high RVP tend to have lower temperature limits of flammability. The curve shown in the plot is based on estimates made by Marshall and Schoonveld.⁽¹²⁾ The temperature limits of the 22 baseline gasoline and gasoline/oxygenate blend test fuels compare favorably with the upper temperature limit estimates of Marshall and Schoonveld.⁽¹²⁾ Figure 3-5 shows the effect of RVP on the upper temperature limits of the 22 test fuels, classified by oxygenate blend component. The open symbols represent the high C₄, PPC-based fuels; the filled symbols represent the high C₅ fuels blended at SwRI.

The trend lines in Figure 3-5 are least squares fits. (The coefficients for these least squares regressions are provided in Appendix E.) The figure shows that the upper temperature limits of flammability of the base/MTBE blends are on average only 1.3°F higher than the upper temperature limits of the baseline gasolines over the range of 6.5

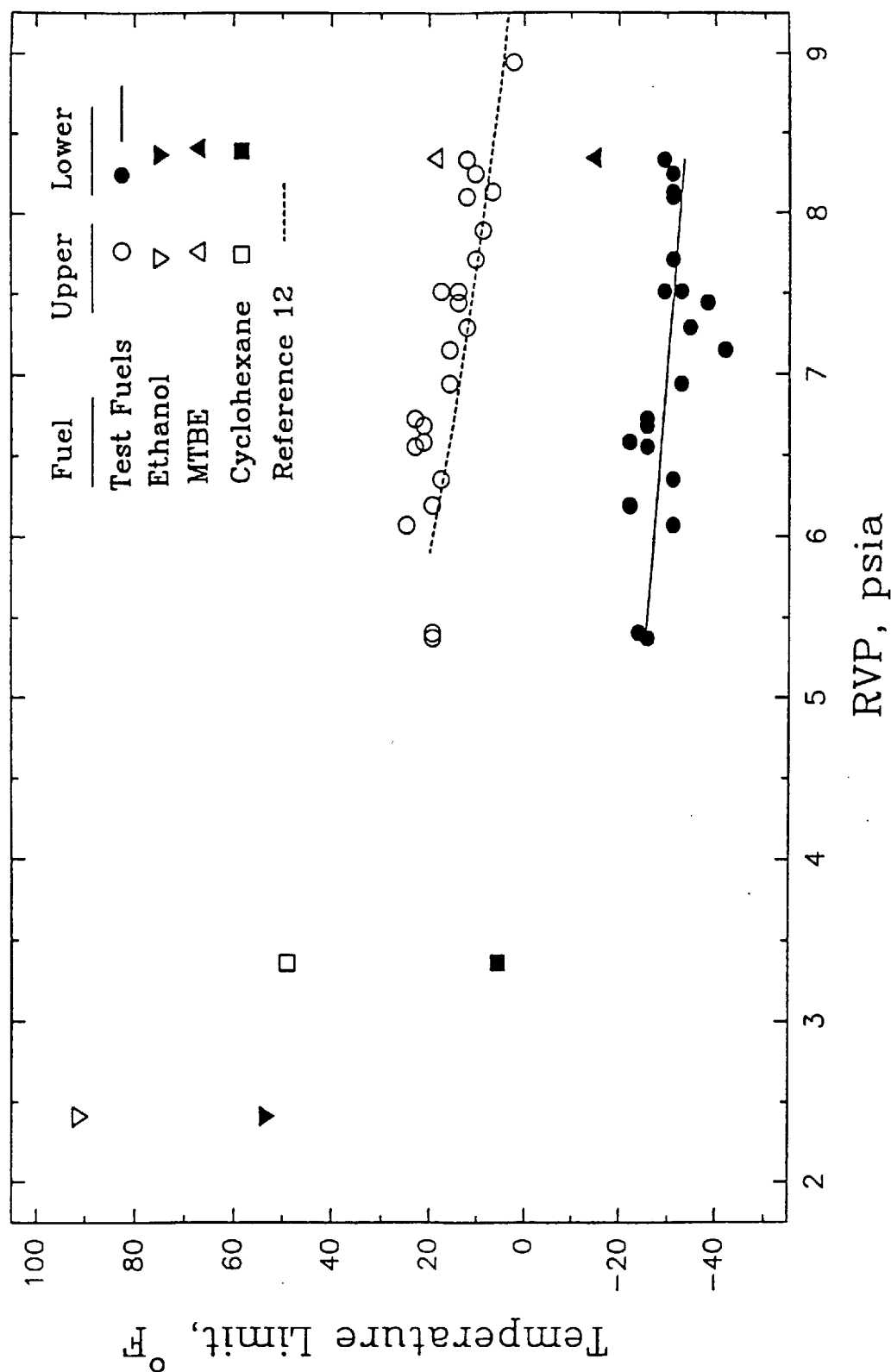
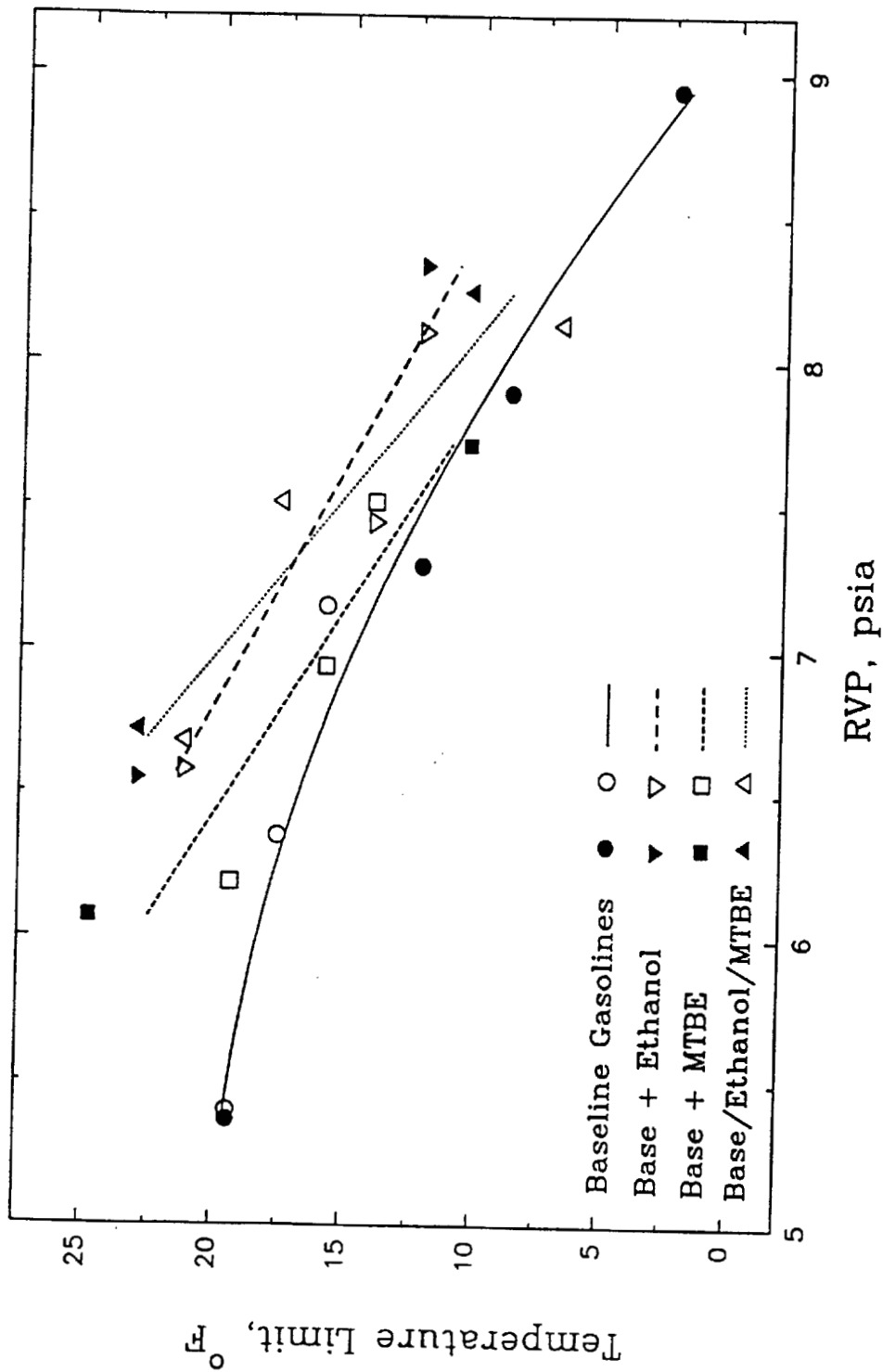


Figure 3-4. The effect of RVP on the upper and lower temperature limits of flammability of all the test fuels



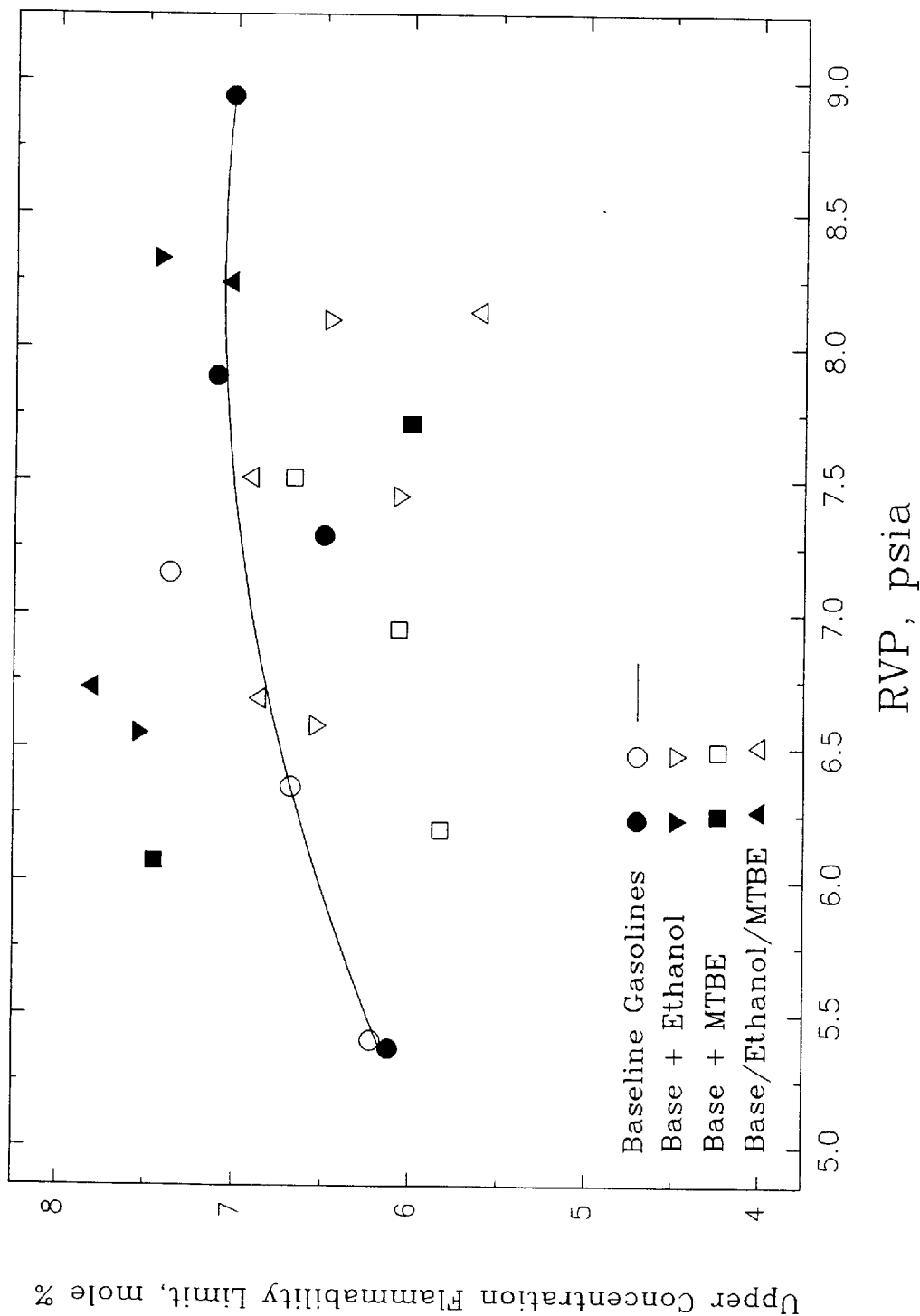
(Filled symbols are high C₅ fuels prepared by SwRI. Open symbols are high C₄ fuels prepared by PPC.)

Figure 3-5. The effect of RVP on the upper temperature limits of flammability of the gasoline test fuels

to 8.0 psi RVP. Furthermore, the upper temperature limits of the fuels containing ethanol are 4.3°F higher on average than those of the baseline gasolines over the same RVP range. The increases in upper flammability limits resulting from the addition of oxygenates were not evaluated for statistical significance. The results are, however, consistent with the understanding that oxygenates have wider flammability limits than neat hydrocarbons. The indications are that MTBE has only a small effect while ethanol appears to raise the upper temperature limit of flammability more substantially. MTBE tends to raise the temperature limits at low RVP but has little effect, if any, at RVPs greater than 7 psia. It should be noted that the departure of the regression line for the MTBE-blended fuels from the temperature limit curve for the baseline gasolines is strongly dependent on the test results for fuel FL2407B. Further investigation would be required to determine whether the measured temperature limit for fuel FL2407B is reliable.

The addition of MTBE to the baseline gasoline FL2407 to produce fuel FL2407B had a stronger impact on the upper temperature limit of flammability than did the addition of MTBE to FL2223 to create the oxygenated blend of similar RVP, fuel FL2223B. This disparity was not observed in the fuels containing ethanol (FL2407A and FL2407C; FL2223A and FL2223C). The basic difference between the FL2407 and the FL2223 fuel groups is that the latter had a much higher C_5 -to- C_4 ratio than the former. Whether or not the difference in C_5 -to- C_4 ratio influenced the flammability of FL2407B is, however, purely speculative.

Figure 3-6 shows the effect of RVP on the calculated upper concentration limits of flammability. The curved line shown in the figure is a polynomial fit of the data on the seven baseline gasolines. It is intended only to serve as a reference for evaluating the effects of changes in fuel composition relative to the baseline gasolines. The non-linearity of the polynomial fit reflects the dependence of the UTLF on vapor composition as well as vapor pressure. The vapor generated from low RVP fuels will contain a greater proportion of higher molecular weight hydrocarbons than the vapors from high RVP fuels. As molecular weight increases, the upper concentration flammability limit decreases. This



(Filled symbols are high C₄ fuels prepared by SwRI. Open symbols are high C₄ fuels prepared by PPC. The curve through the upper concentration limits is a polynomial fit of the seven baseline gasolines.)

Figure 3-6. Calculated upper concentration limits of flammability of the test fuels

is illustrated in Figure 3-6 which shows that the UCLF for the baseline fuels drops in a non-linear fashion as RVP is reduced.

There are no indications in Figure 3-6 that either the temperature limits or the concentration limits are significantly affected by the ratio of C_5 -to- C_4 components in the fuels. In addition, Figure 3-6 also indicates that there is no particular trend in the calculated UCFL data related to oxygenate type in comparison to the baseline gasolines. If anything, the base + MTBE blends tend to have lower concentration limits than the baseline gasolines, except for the PPC fuel FL2407B with 15 vol % MTBE and an RVP of 6.07 psi. (As noted above, fuel FL2407B also appears to generate an unusual result for the upper temperature flammability limit.) It is important to note, however, that this observation is based on calculated values of the UCLF (from the vapor pressure versus temperature relationships at the UTLF). A more definitive finding concerning oxygenate effects must be based on empirical measurements of the UCLF. These measurements are a key element of Phase II of the study (and are presented and discussed in Section 4 of this report).