VAPOR PRESSURE INTERACTIONS OF ETHANOL WITH BUTANE AND PENTANE IN GASOLINE

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ABSTRACT

The utility of ethanol as a fuel component is hampered by the greater than linear contribution it makes to the vapor pressure of resulting fuel blends. Careful measurements were made to see whether RVP control *via* addition of pentane resulted in the same nonlinear vapor pressure effect as observed for the usual component used to control moreover vapor pressure, butane. Within the resolution of the pressure measurements, *no difference* was detected. The result was the same for RVP control with a mixture of butane and pentane.

INTRODUCTION

The Clean Air Act Ammendments of 1990 require the production of reformulated gasoline (RFG) for ozone non-attainment areas starting in 1995. Volatility of RFG is a concern because of two requirements of the law and associated regulations:

- RFG must contain at least 2.0 weight percent oxygen from alcohol or ether.
- Performance standards include reduction in both volatile organic compounds (VOC) and toxic emissions and must not increase nitrogen oxides.

These requirements attempt to drive alcohol concentration in opposite directions under some circumstances. Some oxygenates, including ethanol, increase volatility and in turn cause an increase in evaporative VOC emissions. The contribution of ethanol to volatility of gasoline blends is higher than would be expected based on the pure component vapor pressure of ethanol. Diluted in a predominantly hydrocarbon mixture as in gasoline, the ethanol loses the hydrogen bonding enjoyed by the OH- groups in the neat liquid and exhibits a nonlinear or *excess* vapor pressure.

In the last year, casual observations in various places refocused attention on the factors which affect vapor pressure of ethanol in gasoline blends. Specifically the differential of butane versus pentane RVP control in gasohol mixtures was of interest. The current work used careful measurements of RVP interactions of butane with ethanol or pentane with ethanol in unleaded gasoline to demonstrate ethanol's vapor pressure behavior.

PROCEDURES

A commercial gasoline (regular, summergrade purchased in San Antonio, Texas) was dependanized for use as the base stock in a test of RVP for several ethanol/gasoline mixtures. Dependanized gasoline was selected as the starting material to provide a full range of hydrocarbon types with which ethanol might interact to lower or raise the RVP of the blend. The experimental mixtures of base stock were made with butane alone, with pentane alone, or with butane and pentane to target RVP's (at standard 100°F) of 7 PSI and 8 PSI. These blends and the base gasoline were mixed with ethanol at 10 V%. This matrix is described in Table 1.

The work was done in a laboratory cold room (ambient temperature 35°F) with USP ethanol, reagent pentane, and commercial grade, normal butane. The cold lab was inherently dry, but no special precautions were taken to measure or control water content of the blends. The 8 RVP blends were made first and RVP was measured manually by ASTM D323. Later when the 7 RVP blends were made, both 7 and 8 RVP blends were measured by ASTM D5191 which is an automatic, instrumental method for RVP measurements using a Petrolab Grabner vapor pressure tester.

RESULTS

The results are conclusive, showing the differences in RVP highlighted in Figure 1. The bars represent RVP with and without ethanol, and for 8 RVP samples, the D323 and D5191 results were averaged. For every case studied, the ethanol produced an increase at 100°F (standard RVP temperature) around the average 1.13 PSI.

The behavior shown by the flat RVP difference line in the butane and pentane plots Figures 2 and 3, indicates that identity or concentration of the high volatility component(s) does not affect RVP (within the repeatability of the method, ±0.16 PSI). For measurements at 70°F and 130°F, the differences in vapor pressure are proportionately scaled as shown in Figures 4 and 5. The RVP differences cluster around 1.13 to 1.25 PSI at 100°F, the temperature at which the target blend compositions were calculated.

SUMMARY

No trend arising from identity of pressurizing agent (butane, pentane, or their blends) was observed in the vapor pressure increase arising from the 10 V% ethanol addition in the gasoline samples tested. The results for RVP difference with and without ethanol are as follows:

AVERAGE RVP INCREASE, PSI					
Base	Butane Blends		Pentane Blends		$C_4 + C_5$
Gasoline	7 RVP	8 RVP	7 RVP	8 RVP	8 RVP
1.14	1.20	1.15	1.25	1.10	0.94

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TABLE 1. RVP Measurements: Ethanol + Base Gasoline With or Without Butane or Pentane RVP Estimates by ASTM D 5191 (Mini-Method gives RVPE ±0.12 PSI)

Description		Composition				Sample ID	Temperature		
		Basestock	Butane	Pentane	EtOH		70°F	100°F	130°F
Depentanized Gasoline 1		100	--	--	--	Base 1	(1.28) *	(3.57) *	--
Simulated 8 RVP Gasoline	$C_4 + C_5$	74.65	4.79	20.55	0	Blend 2	4.99	8.82	14.39
	C_5	8.82	--	41.18	0	Blend 3	4.63	8.51	14.30
	C_4	90.74	9.26	--	0	Blend 4	5.03	8.67	13.58
8 RVP Samples • 10 V% ethanol	with base gasoline	90	--	--	10	Blend 5 Base + EtOH	2.04	4.57	8.85
	Blend 2	Blend 2 90V%			10	Blend 6	5.38	9.95	17.11
	Blend 3	Blend 3 90V%			10	Blend 7	5.29	10.11	17.84
	Blend 4	Blend 4 90V%			10	Blend 8	5.55	9.89	16.46
Depentanized Gasoline 2		100	--	--	--	Base 2	2.23	4.34	7.63
with 10 V% Ethanol		90	--	--	10	Base 2 + EtOH	2.65	5.62	10.37
Simulated 7 RVP	C_4	94.83 V%	5.17 V%	--	0	Blend 9	4.03	7.00	11.38
	C_5	68.55 V%	--	31.45	0	Blend 10	3.78	7.00	11.82
7 RVP Samples + 10 V% Ethanol	Blend 9	Blend 9 90.0 V%		--	10.0	Blend 11	4.33	8.18	14.11
	Blend 10	Blend 10 90.0 V%		--	10.0	Blend 12	4.22	8.25	14.67

* Calculated from Manual ASTM D 323

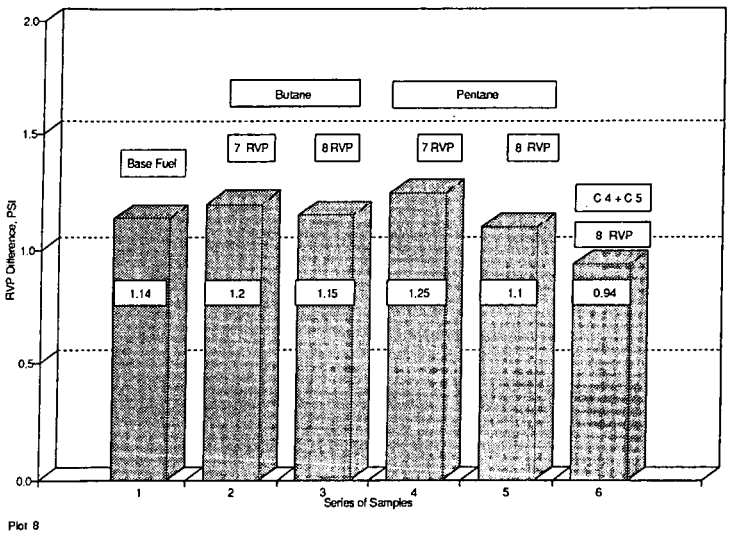

FIGURE I. RVP DIFFERENCES
Neat vs. Ethanol Blends

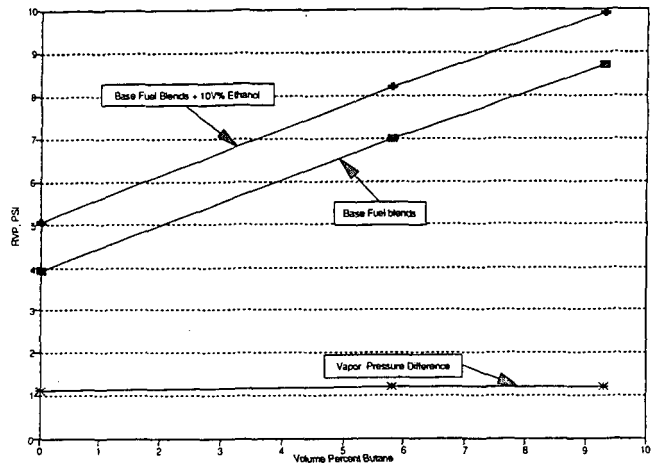

FIGURE 2. RVP VS. PERCENT BUTANE (100)

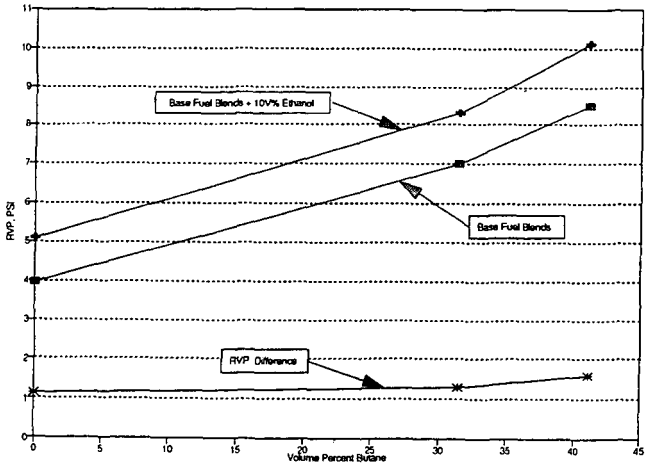

FIGURE 3. RVP VS. PERCENT PENTANE (100)

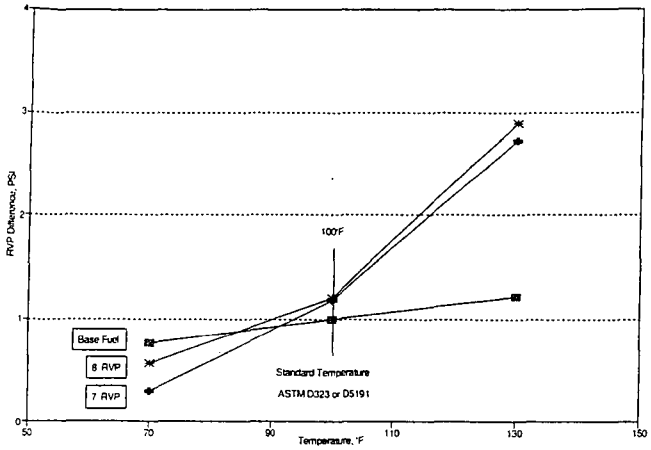

FIGURE 4. RVP DIFFERENCE VS. TEMPERATURE
Blends made with Butane

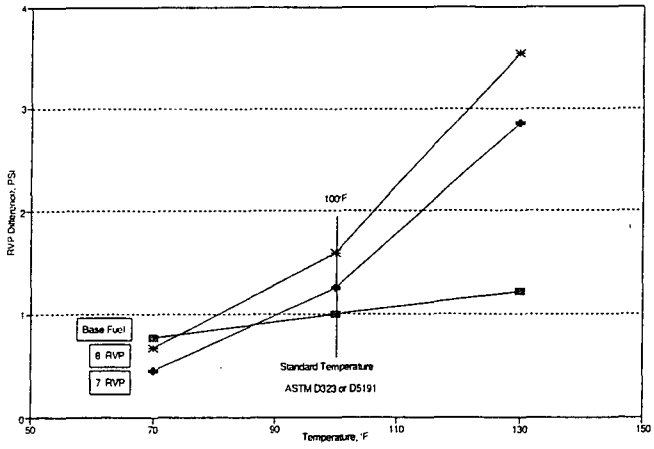

FIGURE 5. RVP DIFFERENCE VS. TEMPERATURE
Blends made with Pentane