



Property Analysis of Ethanol– Natural Gasoline–BOB Blends to Make Flex Fuel

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Technical Report
NREL/TP-5400-67243
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Prepared under Task No. WFGS.1000

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List of Acronyms

ASTM	ASTM International
BOB	blendstock for oxygenate blending (generic)
CARBOB	California reformulated blendstock for oxygenate blending
DHA	detailed hydrocarbon analysis
E _{xx}	ethanol content in blend, where xx is the percent ethanol by volume
g/mol	grams per mole
ppm	parts per million by mass
psi	pounds per square inch
RBOB	reformulated blendstock for oxygenate blending
RVP	Reid vapor pressure
vol%	percent by volume
wt%	percent by weight

Executive Summary

The purpose of this study was to evaluate the potential expansion of the Reddy Reid vapor pressure (RVP) model (Reddy 2007) to estimate the RVP of ethanol fuel blends when natural gasoline is used as a blendstock. The U.S. Environmental Protection Agency recently proposed that the Reddy model could be used to demonstrate compliance with proposed maximum RVP requirements for E16–E83 ethanol blends made at terminals (U.S. Environmental Protection Agency 2016). Ten natural gasolines were analyzed for a wide range of properties, including RVP, benzene and aromatic content, sulfur, distillation, stability, and metals to determine their quality. Four of these samples were selected to blend with a blendstock for oxygenate blending and ethanol to produce E51, E70, and E83 blends, targeting 7.8- and 9.0-psi RVPs for the finished fuels. The Reddy model was based on two component blends, and this work assumed that the blendstock for oxygenate blending and the natural gasoline blended linearly and could be treated as a single hydrocarbon input into the Reddy calculations. The Reddy model was then used to estimate the volume of hydrocarbon needed to produce the target ethanol blends. Results show that the Reddy model adequately predicts the RVP of the finished blend for E51 but significantly underestimates the RVPs of E70 and E83 blends. It is hypothesized that the underprediction is a function of the very low aromatic content of the E70 and E83 blends compared to the blendstocks for oxygenate blending used by Reddy to develop the model. It is recommended that future work consider additional samples to further validate these conclusions.

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1 Introduction

In 2015, ethanol production in the United States was 14.8 billion gallons (U.S. Energy Information Administration 2016a) and gasoline consumption was 140.43 billion gallons (U.S. Energy Information Administration 2016b), with imports of roughly 100 million gallons. A vast majority of the fuel-grade ethanol is blended into gasoline at 10 volume percent (vol%), also known as E10, and represents over 95% of the domestic gasoline market (U.S. Energy Information Administration 2016c). A small amount of ethanol is used in higher-level blends with gasoline as E15, ethanol fuel blends (E16–E50), and Flex Fuel, although these volumes are quite small compared to the volume of E10 in the market.

The highest ethanol content fuel in the market is Flex Fuel with 51 vol%–83 vol% ethanol in a balance of hydrocarbons, usually gasoline blendstocks. The quality of Flex Fuel is specified in ASTM¹ D5798, Standard Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines, which has undergone significant changes in recent years in an effort to improve fuel quality. The most important of these changes has been the addition of a fourth volatility class for wintertime fuels and a wider allowance of ethanol content throughout the year, giving blenders maximum flexibility to meet the specifications.

The U.S. Department of Energy’s National Renewable Energy Laboratory and the Coordinating Research Council have conducted several surveys of Flex Fuel in recent years (Alleman et al. 2009, Alleman 2011a, Alleman 2011b, Williams and Alleman 2014, Alleman 2015). A common finding in these surveys has been the low vapor pressure (Reid vapor pressure, or RVP) of the samples. The low RVP, found year round in these studies, would lead to immediate driveability and cold start problems.

The low RVP of Flex Fuel is likely due to the strong effect of ethanol on the vapor pressure of the blend. As ethanol content increases, the vapor pressure drops rapidly—examples are provided in the appendix of D5798. It is hypothesized that Flex Fuel samples in the previous studies used hydrocarbon blendstocks with lower than the required RVP.

The RVP of a two-component hydrocarbon-ethanol blend can be estimated with the Reddy model (Reddy 2007). The model has been applied to a wide range of ethanol blends with blendstocks for oxygenate blending (BOBs) (Christensen et al. 2011) and has been included in D5798. Reddy states that the model was based on the UNIFAC (universal quasichemical functional group activity coefficients) method and used as inputs the RVP of the hydrocarbon and the volume percent of ethanol. Applying this model to the previous Flex Fuel survey data, it becomes clear that to reach the target RVP, samples needed to be blended with higher RVP blendstocks. In fact, Alleman (2015) hypothesizes that some of the samples in the most recent Flex Fuel study used natural gasoline as a high-RVP blendstock in some Flex Fuel.

One of the first steps to using natural gasoline as the blendstock in Flex Fuel is setting minimum quality requirements to ensure that the finished fuels meet expected quality parameters. ASTM recently published D8011, a specification for using natural gasoline as a blendstock in ethanol blends. The specification sets a maximum distillation temperature and also requires that the natural gasoline meet the requirements set forth in D5798 for blendstocks for Flex Fuel.

¹ All test methods and specifications are ASTM International (ASTM) unless otherwise specified.

The goal of this study is to determine if the Reddy model can be expanded to predict the RVP of a Flex Fuel that is composed of ethanol, natural gasoline, and a BOB. If the Reddy model can estimate, with sufficient precision and accuracy, the RVP of the finished blend, the model could be applied by blenders seeking to use natural gasoline as a blendstock component for producing Flex Fuel blends. The use of the model could eliminate costly and time-consuming testing of each fuel batch to determine the RVP of the blend. The model would have to be protective, so that any errors would produce a modeled RVP higher than would be found through analytical testing.

To achieve this goal, several natural gasoline samples were collected from the market along with two representative BOBs and denatured fuel ethanol. The samples were tested for key analytical properties. Using the Reddy model as a tool to estimate the composition yielding a target vapor pressure, Flex Fuel blends of E51, E70, and E83 were produced, targeting maximum blend vapor pressures of 7.8 psi and 9.0 psi. The RVPs of the finished blends were measured and compared to the RVPs estimated by the Reddy model.

2 Materials and Methods

2.1 Natural Gasoline, Ethanol, and Hydrocarbon Blendstocks

A total of 10 natural gasoline samples were collected between January and June 2015 for this study. Samples were selected to represent a broad range of natural gasoline quality from raw condensate to denaturant grade natural gasoline. All samples were stored cold in their original containers until needed for analysis.

Three batches of ethanol were used for this project. The same ethanol producer supplied two batches of ethanol during the project. The first sample, used for the E51 and a majority of the E70 blends, was not denatured. The second sample, used for two E70 blends and all the E83 blends, was denatured. The exact denaturant was unknown and assumed to be natural gasoline with a 13.5-psi RVP based on information provided by the ethanol producer. A chemical grade 200-proof ethanol was purchased from Sigma Aldrich and used to make two validation E83 blends.

A petroleum refiner provided two hydrocarbon BOBs for this project. Both BOBs were typical market samples used in summertime gasoline. One sample was a California reformulated BOB (CARBOB), typical of those used in the California market. The other sample was a reformulated BOB (RBOB), typical of those used in reformulated gasoline markets throughout the country.

2.2 Test Methods

All testing was conducted following ASTM test methods. The specific methods used are provided with the results. The natural gasoline samples were tested for vapor pressure, octane number, sulfur, benzene and aromatics, distillation, metals, corrosion, and stability. The BOBs were tested for vapor pressure, octane number, sulfur, benzene and aromatics, and distillation. A detailed hydrocarbon analysis (DHA) was performed on all the natural gasoline and BOB samples. The ethanol was tested for acidity, sulfur, water, pHe, chloride, and sulfate.

Four of the 10 natural gasolines were selected for blending with a BOB and ethanol to produce Flex Fuel blends. Blends of natural gasoline, a BOB, and ethanol were made volumetrically by hand in a cold room. The study targeted E51, E70, and E83 to cover the range of ethanol content in Flex Fuel in the market. All blends were tested for ethanol content, water, and vapor pressure after blending.

2.3 Vapor Pressure Modeling

The measured vapor pressures were compared to the estimated vapor pressure of the blends using the Reddy model (Reddy 2007). The Reddy model assumes a two-component blend of hydrocarbon and ethanol. For this project, the assumption was made that the BOB and natural gasoline would blend linearly on a volumetric basis and this blend could be treated as a single hydrocarbon used as an input into the Reddy model, using equation 1. Details of the Reddy model and its application to natural gasoline–ethanol blending have been previously published (Alleman et al. 2015).

$$RVP_{\text{blend}} (\text{psi}) = K_{\text{hydrocarbon}} \times (V_{\text{hydrocarbon}}/100) \times RVP_{\text{hydrocarbon}} + K_{\text{ethanol}} \times (V_{\text{ethanol}}/100) \times 2.4 \quad (1)$$

where:

$$V_{\text{ethanol}} = \text{vol\% ethanol}$$

$$V_{\text{hydrocarbon}} = \text{vol\% hydrocarbon}$$

$$K_{\text{hydrocarbon}} = -7\text{E-}07(V_{\text{ethanol}})^3 + 0.002(V_{\text{ethanol}})^2 + 0.0024(V_{\text{ethanol}}) + 1$$

$$K_{\text{ethanol}} = 46.321(V_{\text{ethanol}})^{-0.8422}$$

3 Results and Discussion

3.1 Analytical Properties

The natural gasolines sampled for this project were widely diverse in their properties. Not all of the samples collected were intended to be blended into Flex Fuel, but were included to examine a spectrum of natural gasoline properties available at the time of the study. Two samples (A and B) were supplied by a midstream company. Samples C, E, F, and I were from natural gas processing plants. Sample D was from a manufactured fuel provider. Samples G, H, and J were denaturants from ethanol producers. All samples were submitted to a third-party testing laboratory and stored cold (temperature of between 3°C–4°C) for the duration of the project.

Table 1 summarizes the compound classes by DHA (D6729-14) in the natural gasolines. The DHA results for the BOBs are given in Table 2. The sum of the individual components will not necessarily equal 100 due to rounding. The most notable difference between the BOBs and natural gasoline samples is the generally higher aromatic content of the BOBs and the more paraffinic composition of the natural gasolines.

Table 1. DHA (D6729-14) of the Natural Gasoline Samples

Group, wt%	Sample									
	A	B	C	D	E	F	G	H	I	J
n-Paraffins	42.3	43.1	39.2	29.3	32.0	38.2	40.4	33.4	35.8	43.2
iso-Paraffins	42.0	43.4	46.1	44.5	35.7	38.3	41.7	37.8	42.0	44.0
Aromatics	1.6	1.4	2.2	8.4	13.6	7.0	6.5	14.1	8.6	2.0
Monoaromatics	1.5	1.4	2.2	8.4	12.0	6.9	6.5	13.7	8.5	2.0
Benzene	0.5	0.6	0.9	4.4	0.8	1.1	1.1	1.1	0.7	0.9
Naphthalenes	0.0	0.0	0.0	0.0	0.6	0.0	0.0	0.0	0.0	0.0
Naphtheno/Olefino-Benzenes	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.2	0.0	0.1
Indenes	0.0	0.0	0.0	0.0	0.9	0.0	0.0	0.2	9.7	0.0
Naphthenes	10.3	8.6	8.8	17.2	9.9	11.3	8.2	8.8	9.7	7.1
Mono-naphthenes	10.3	8.6	8.8	17.2	9.9	11.3	8.2	8.8	9.7	7.1
Di/Bicyclo-naphthenes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Olefins	3.5	3.3	3.0	0.7	3.1	4.8	3.0	4.3	3.1	2.2
n-Olefins	0.1	0.0	0.1	0.0	0.4	0.3	0.2	1.0	0.3	0.0
iso-Olefins	3.2	3.2	2.6	0.6	2.4	4.0	2.6	2.8	2.5	2.2
Naphtheno-Olefins	0.2	0.0	0.1	0.1	0.4	0.5	0.2	0.4	0.0	0.0
di-Olefins	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Oxygenates	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Unidentified	0.3	0.2	0.7	0.0	5.7	0.5	0.4	1.6	0.9	1.4

Table 2. DHA (D6729-14) of BOBs Used in This Study

Group, wt%	Sample	
	CARBOB	RBOB
n-Paraffins	7.0	11.9
iso-Paraffins	48.7	47.2
Aromatics	18.8	31.3
Monoaromatics	18.5	30.3
Benzene	1.1	0.2
Naphthenes	0.1	0.2
Naphtheno/Olefino- Benzenes	1.2	0.5
Indenes	0.1	0.5
Naphthenes	13.8	5.3
Mono-naphthenes	13.8	5.3
Di/Bicyclo-naphthenes	0.0	0.0
Olefins	9.9	3.6
n-Olefins	1.8	1.0
iso-Olefins	6.6	2.3
Naphtheno-Olefins	1.2	0.3
di-Olefins	0.2	0.0
Oxygenates	0.0	0.0
Unidentified	1.8	0.8

Tables 3 and 4 list the property data for the natural gasoline samples and BOBs, respectively. The natural gasolines were analyzed for a wider range of properties to better examine the differences among these diverse samples. The BOBs were not analyzed for metals, stability, silver corrosion, or copper corrosion. Two of the natural gasoline samples were submitted in 1-liter containers, and insufficient sample was available for many of the tests. These samples were omitted from consideration for additional blending due to limited available volume.

The data presented here confirm a previous report on natural gasoline properties (Alleman et al. 2015). The average molecular weights of the samples were determined by weighted average based on molar concentration of the individual components from the DHA. As expected, the Research octane number and Motor octane number for the natural gasoline samples were lower than for a typical BOB (ranging from 41 to 79) due to their highly paraffinic nature. Compared to the BOBs in this study, the natural gasolines were generally lighter and had more low boiling, volatile components.

Benzene content was tested by two methods, D5580-13 and D6729-14, and agreement was very good between the two methods. The aromatic content of the natural gasolines was determined

through DHA, D5580, and D1319 (for samples D, G, H, and J). Good agreement was found between the methods.

Specification D8011 had not been published when these samples were collected. Sample D had benzene content four times the specification limit, and sample E would not meet the specification requirements for final boiling point and silver corrosion.

Table 3. Analytical Property Data for Natural Gasoline Samples

	Method	Sample									
		A	B	C	D	E	F	G	H	I	J
Average Molecular Weight, g/mol	D6729-14	80.9	78.9	79.2	83.2	103.0	89.1	84.4	82.5	71.2	78.4
RVP, psi	D5191-15	12.27	13.18	12.89	10.66	8.23	13.27	15.76	13.74	12.33	13.43
RON	D2699-10	-	-	76	72	41	60	68	79	58	72
MON	D2700-10	-	-	70	71	41	58	64	76	57	70
Sulfur, ppm	D5453-12	101.1	45.6	104.4	29.4	59.0	382.3	186.7	33.0	239.1	21.2
Aromatics, vol%	D1319-15	-	-	-	7.3	-	-	3.9	14.0	-	1.2
Toluene, wt%	D5580-13	-	-	0.85	2.82	2.63	2.93	2.99	3.42	3.30	0.75
Ethyl benzene, wt%		-	-	<0.01	0.15	0.13	0.13	<0.01	0.59	<0.01	<0.01
p-/m-Xylene, wt%		-	-	0.22	0.62	2.37	1.38	1.47	2.44	2.32	<0.01
o-Xylene, wt%		-	-	<0.01	0.20	0.29	0.32	0.26	0.90	0.36	<0.01
C9 aromatics, wt%		-	-	<0.01	<0.01	10.86	0.75	0.40	6.97	1.42	<0.01
Total aromatics, wt%		-	-	1.97	8.28	16.94	6.59	6.16	15.32	8.08	1.62
Benzene, wt%		-	-	0.91	4.49	0.65	1.08	1.05	1.00	0.68	0.88
Benzene, wt%	D6729-14	0.5	0.6	0.9	4.4	0.8	1.1	1.1	1.1	0.7	0.9

	Method	Sample									
		A	B	C	D	E	F	G	H	I	J
Distillation, °C	D86-12										
IBP		-	-	30	32	33	30	27	29	28	32
T10		-	-	39	46	64	50	37	37	48	39
T50		-	-	48	62	124	82	72	58	88	45
T90		-	-	86	102	287	121	116	135	133	76
FBP		-	-	120	138	353	161	160	197	181	111
Silver Strip Corrosion	D4814-15 Annex 1	-	-	0	0	2	1	0	0	0	0
Copper Strip Corrosion	D130-12	-	-	1A	1A	1A	1A	1A	1A	1A	1A
Elemental analysis, ppm	D7111-11	-	-								
Al		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Sb		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ba		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
B		-	-	<0.2	<0.2	0.4	<0.2	<0.2	<0.2	<0.2	<0.2
Ca		-	-	<0.2	<0.2	<0.2	1.2	0.6	<0.2	4.2	<0.2
Cr		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cu		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Fe		-	-	<0.2	<0.2	0.2	0.8	0.6	<0.2	1	<0.2
Pb		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Mg		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Mn		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Mo		-	-	<0.2	<0.2	<0.2	0.8	0.6	<0.2	2	<0.2
Ni		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
P		-	-	<0.2	<0.2	<0.2	1.6	0.8	<1	2.4	<0.2
Si		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ag		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Na		-	-	<1	<1	<1	2.6	1.8	1.4	2.4	3.6
Sn		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Zn		-	-	<0.2	<0.2	<0.2	0.8	0.2	<1	1.4	<0.2
K		-	-	<1	<1	<1	<1	<1	<1	<1	<1
Sr		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

	Method	Sample									
		A	B	C	D	E	F	G	H	I	J
V		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ti		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cd		-	-	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Stability	D525-12a	-	-								
Run time, min		-	-	1,440	1,440	1,440	1,440	1,440	1,440	1,440	1,440
Break		-	-	No break	No break	No break	No break	No break	No break	No break	No break
Break Point		-	-	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Max pressure, psi		-	-	166.1	158.8	146.4	150.6	164.1	161	148.8	160.3
Max Time, min		-	-	546	737	486	178	452	806	502	1440
Min pressure, psi		-	-	165.6	158	145.1	129.1	160.5	154	147.8	159.4
Min time, min		-	-	762	387	201	1,439	1,440	1,440	1,299	316
Pressure drop, psi		-	-	0.5	0.8	1.3	21.5	3.6	7	1	0.9

MON: Motor octane number
RON: Research octane number

Table 4. Analytical Property Results for BOB Samples

	Method	Sample	
		CARBOB	RBOB
Average Molecular Weight, g/mol	D6729-14	99.8	99.4
RVP, psi	D5191-15	6.17	5.59
RON	D2699-10	85	86
MON	D2700-10	81	81
Sulfur, ppm	D5453-12	11.4	5.9
Benzene, wt%	D5580-13	1.06	0.15
Benzene, wt%	D6729-14	1.1	0.2

	Method	Sample	
		CARBOB	RBOB
Distillation, °C	D86-12		
IBP		41	40
T10		65	67
T50		106	102
T90		156	159
FBP		198	200

IBP: initial boiling point
FBP: final boiling point

The properties of the ethanol used in blending are presented in Table 5. The project intent was to use undenatured fuel ethanol for blending to eliminate any impact of denaturant in the ethanol. For the first batch, the ethanol was not denatured, as requested. The volume of the first batch was not sufficient for the entire project (discussed later), and a second batch was requested from the same ethanol producer. Although the request was made for an undenatured sample, a denatured sample was provided. The measured ethanol content was 96.81 vol%, with a denaturant content of 3.19 vol%. The ethanol producer was asked if information could be provided about the denaturant, but that information was unavailable for this batch of ethanol. Average denaturant properties at the plant were available and assumed to be typical of this batch of denatured ethanol. It was assumed that it was denatured with natural gasoline having an RVP of 13.5 psi. A third sample of laboratory-grade 200-proof ethanol was used in two samples.

Table 5. Ethanol Properties

Property	Method	Ethanol Batch 1	Ethanol Batch 2	200-proof Ethanol
Acidity, mg KOH/g	D1613-06	0.0253	0.0318	
Sulfur, ppm	D5453-12	1.8	1.9	
Water, mass%	D6304-07	0.6407	0.9291	0.4640
pHe	D6423-14	4.0	7.4	
Chloride, ppm	D7328-13	0.9	<0.1	
Sulfate, ppm		1.4	1.1	
Potential sulfate, ppm		1.5	1.2	
RVP	D5191-15	2.2?	3.5	2.2
Ethanol content, vol%	D5501-12ε1	100	96.81	100

3.2 Selection of Samples for Blending

Not all of the natural gasolines collected in this study were blended with ethanol. The National Renewable Energy Laboratory and the U.S. Environmental Protection Agency discussed the properties of the samples and selected D, E, G, and J for testing. These samples represented a range of RVP and aromatic contents. In particular, sample J was selected for its very low aromatic content of 1.62 percent by weight (wt%). Figure 1 shows a picture of sample E from the test laboratory. The overall low quality of the sample, including haziness and high amounts of free water, removed it from consideration for this project, and sample H was selected as an alternative.



Figure 1. Photograph of sample E after receipt

Photo by Melissa Legg, Southwest Research Institute

The third-party testing laboratory was instructed to produce volumetric hand blends of the samples to produce the target Flex Fuel blends. Blends were made in a cold room, and samples never left the cold room until needed for testing. Most of the blends were produced as three-component blends, though at higher ethanol contents only natural gasoline and ethanol were used to produce the blend. The blends were produced by volume, where each component was measured separately via pipette and added to the container one at a time.

It was assumed that the hydrocarbons blended linearly and could be treated as a single input into the Reddy model (Reddy 2007). The methodology assumes that the mole fraction is roughly

equal to the volume fraction of each component, making an ideal mixture of non-polar components.

A spreadsheet was developed to determine the maximum volume of natural gasoline for each blend at the target ethanol content. Tables 6–8 present the volumes of each component used for the blending at the analytical laboratory, based on this modification of the Reddy model. The laboratory was instructed to blend to integer volumes, as shown in Tables 6–8. The calculation from the model provided additional precision that was not practical to use for this study. For example, the laboratory analyst was instructed to blend with 23 vol% natural gasoline, although the model might determine that 22.86 vol% was needed to meet the vapor pressure target.

Table 6. Blending Targets to Produce E51 Blends with Natural Gasoline, BOB, and Ethanol

Target RVP, psi	Natural Gasoline, sample	BOB	Natural Gasoline of Blend (vol%, approximate)	BOB in Blend (% , approximate)
7.8	D	CARBOB	14	35
7.8	D	RBOB	18	31
7.8	G	CARBOB	6	43
7.8	G	RBOB	9	40
7.8	H	CARBOB	8	41
7.8	H	RBOB	11	38
7.8	J	CARBOB	8	41
7.8	J	RBOB	11	38
9.0	D	CARBOB	31	18
9.0	D	RBOB	33	16
9.0	G	CARBOB	14	35
9.0	G	RBOB	16	33
9.0	H	CARBOB	18	31
9.0	H	RBOB	20	29
9.0	J	CARBOB	18	31
9.0	J	RBOB	21	28

Table 7. Blending Targets to Produce E70 Blends with Natural Gasoline, BOB, and Ethanol

Target RVP, psi	Natural Gasoline, sample	BOB	Natural Gasoline of Blend (vol%, approximate)	BOB in Blend (% , approximate)
7.8	D	CARBOB	24	6
7.8	D	RBOB	25	5
7.8	G	CARBOB	11	19
7.8	G	RBOB	12	18
7.8	H	CARBOB	14	16
7.8	H	RBOB	15	15
7.8	J	CARBOB	14	16
7.8	J	RBOB	15	15
9.0	D	CARBOB	30	0 ^a
9.0	D	RBOB	30	0 ^a
9.0	G	CARBOB	17	13
9.0	G	RBOB	18	12
9.0	H	CARBOB	22	8
9.0	H	RBOB	23	7
9.0	J	CARBOB	23	7
9.0	J	RBOB	23	7

^a Predicted RVP is 8.3 psi

Table 8. Blending Targets to Produce E83 Blends with Natural Gasoline, BOB, and Ethanol

Target RVP, psi	Natural Gasoline, sample	BOB	Natural Gasoline of Blend (vol%, approximate)	BOB in Blend (% , approximate)
7.8	D	CARBOB	17	0 ^a
7.8	D	RBOB	17	0 ^a
7.8	G	CARBOB	16	1
7.8	G	RBOB	16	1
7.8	H	CARBOB	17	0 ^b
7.8	H	RBOB	17	0 ^b
7.8	J	CARBOB	17	0 ^c
7.8	J	RBOB	17	0 ^c
9.0	D	CARBOB	17	0 ^a
9.0	D	RBOB	17	0 ^a

Target RVP, psi	Natural Gasoline, sample	BOB	Natural Gasoline of Blend (vol%, approximate)	BOB in Blend (% , approximate)
9.0	G	CARBOB	17	0 ^b
9.0	G	RBOB	17	0 ^b
9.0	H	CARBOB	17	0 ^d
9.0	H	RBOB	17	0 ^d
9.0	J	CARBOB	17	0 ^c
9.0	J	RBOB	17	0 ^c

^a Predicted RVP is 6.2 psi

^b Predicted RVP is 7.3 psi

^c Predicted RVP is 7.2 psi

^d Predicted RVP is 8.1 psi

For two of the E70 blends at 9.0 psi and almost all of the E83 blends, the Reddy model estimates that the RVP of the finished blend will be below the target RVP even when the maximum amount of natural gasoline is used as the blendstock. This is especially true for the higher ethanol blends, where even small changes in ethanol content can have large impacts on vapor pressure. It was impossible to meet the RVP target using with the higher vapor pressure natural gasolines making up the entire hydrocarbon portion. At these high ethanol concentrations, the low vapor pressure of ethanol dominates the blend RVP.

3.3 Blend Results

Tables 9–11 present the analytical results for the E51, E70, and E83 blends. The RVP, ethanol, and water contents were measured directly. The overall aromatic content of the blend was calculated from the aromatic content of the natural gasoline and BOB, based on the blending target volumes in Tables 6–8, respectively and an estimated aromatic content of 2.3% in the denaturant in ethanol batch 2.

The predicted RVP was determined by adjusting the Reddy model for the measured ethanol content in the sample. The ratios of natural gasoline and BOB were adjusted proportionally. To illustrate, if the ratio of natural gasoline to BOB was 2:1 for an E70 and the measured ethanol content was 71, it was assumed that the 2:1 ratio of natural gasoline to BOB was maintained to produce 29 vol% in the hydrocarbon portion of the blend. These values were then used to calculate the predicted RVP.

Table 9. Results of Natural Gasoline–BOB–Ethanol Blending for E51

Target RVP, psi	Blendstock	Measured RVP, psi	Predicted RVP using actual ethanol content, psi	Predicted – measured RVP, psi	Measured ethanol content, vol%	Water content, vol%	Aromatic content, vol%
7.8	D / CARBOB	7.50	7.6	0.1	51.92	0.3098	8.0
7.8	D / RBOB	7.63	7.6	0.0	51.69	0.3127	11.0
7.8	G / CARBOB	7.29	7.5	0.3	52.99	0.3130	8.5

Target RVP, psi	Blendstock	Measured RVP, psi	Predicted RVP using actual ethanol content, psi	Predicted – measured RVP, psi	Measured ethanol content, vol%	Water content, vol%	Aromatic content, vol%
7.8	G / RBOB	7.35	7.7	0.3	51.9	0.3137	12.8
7.8	H / CARBOB	7.43	7.5	0.1	52.23	0.3068	9.2
7.8	H / RBOB	7.33	7.6	0.3	52.07	0.3063	13.2
7.8	J / CARBOB	7.57	7.6	0.1	52.02	0.3126	8.0
7.8	J / RBOB	7.60	7.6	0.0	52.12	0.3100	11.8
9.0	D / CARBOB	9.23	8.8	-0.5	52.56	0.3162	6.0
9.0	D / RBOB	9.08	8.8	-0.3	52.03	0.3113	7.6
9.0	G / CARBOB	8.69	8.7	0.1	52.96	0.3144	7.5
9.0	G / RBOB	8.30	8.7	0.4	51.98	0.3116	11.1
9.0	H / CARBOB	8.88	8.7	-0.2	53.02	0.3151	8.6
9.0	H / RBOB	8.62	8.7	0.1	51.71	0.3080	12.0
9.0	J / CARBOB	9.17	8.7	-0.4	52.25	0.3101	6.3
9.0	J / RBOB	9.08	8.8	-0.3	51.73	0.3055	9.0

Table 10. Results of Natural Gasoline–BOB–Ethanol Blending for E70

Target RVP, psi	Blendstock	Measured RVP, psi	Predicted RVP using actual ethanol content, psi	Predicted – measured RVP, psi	Measured ethanol content, vol%	Water content, vol%	Aromatic content, vol%
7.8	D / CARBOB	8.3	7.3	-0.9	72.96	0.4188	2.9
7.8	D / RBOB	8.3	7.4	-0.9	72.56	0.4226	3.4
7.8	G / CARBOB	7.5	7.1	-0.4	74.60	0.4176	3.8
7.8	G / RBOB	7.7	7.2	-0.5	73.58	0.4137	5.6
7.8	H / CARBOB	8.0	7.2	-0.8	73.84	0.4158	4.7
7.8	H / RBOB	7.9	7.3	-0.6	72.80	0.4194	6.3
7.8	J / CARBOB	8.5	7.2	-1.3	73.87	0.4193	3.0
7.8	J / RBOB	8.4	7.4	-1.1	72.49	0.4231	4.4
9.0	D	8.7	8.0	-0.7	72.05	0.4234	2.3
9.0	D	8.6	8.0	-0.6	71.94	0.4236	2.3
9.0	G / CARBOB	8.8	8.2	-0.6	74.51	0.4138	3.0
9.0	G / RBOB	8.67	8.3	-0.4	73.81	0.4168	4.2
9.0	H / CARBOB	9.1	8.3	-0.8	73.59	0.4082	4.4
9.0	H / RBOB	9.3	8.5	-0.8	72.90	0.4211	5.2
9.0	J / CARBOB ^a	10.3	9.1	-1.2	69.70	0.6837	1.6
9.0	J / RBOB ^a	10.2	9.2	-1.0	69.30	0.6828	2.1

^a Samples blended with ethanol batch 2

Table 11. Results of Natural Gasoline–BOB–Ethanol Blending for E83; All Samples Blended with Ethanol Batch 2

Target RVP, psi	Blendstock	Measured RVP, psi	Predicted RVP using actual ethanol content, psi	Predicted – measured RVP, psi	Measured ethanol content, vol%	Water content, vol%	Aromatic content, vol%
7.8	D	7.21	6.5	-0.7	81.7	0.7840	1.4%
7.8	D	7.32	6.5	-0.7	81.5	0.7738	1.4%
7.8	G	8.37	7.9	-0.5	82.2	0.7896	1.2%
7.8	G	8.4	7.9	-0.5	82.0	0.7963	1.3%
7.8	H / CARBOB	8.34	7.6	-0.7	81.6	0.7777	2.5%
7.8	H / RBOB	8.26	7.6	-0.7	81.9	0.7795	2.4%
7.8	J	9.17	7.5	-1.6	81.6	0.7765	0.3%
7.8	J	9.13	7.5	-1.6	81.6	0.7894	0.3%
9.0	D	7.21	6.6	-0.6	81.6	0.7705	1.4%
9.0	D	7.21	6.6	-0.6	81.5	0.7852	1.4%
9.0	G	8.26	8.1	-0.1	82.3	0.7707	1.0%
9.0	G	8.31	8.2	-0.1	82.2	0.7900	1.0%
9.0	H	8.43	7.6	-0.8	81.8	0.7766	2.5%
9.0	H	8.52	7.7	-0.8	81.4	0.7915	2.5%
9.0	J	9.08	7.5	-1.6	81.9	0.7817	0.3%
9.0	J	8.98	7.5	-1.4	81.6	0.7883	0.3%

The RVP results from the E70 and E83 blends were considerably higher than expected based on the Reddy model estimation. The RVPs of the natural gasolines were retested to determine if the samples changed over the course of the project. Testing determined that the RVP of sample H had decreased significantly over the course of the project, and D had changed slightly. A comparison of the low boiling compounds by DHA in the natural gasolines did not reveal significant differences in the compounds present between the four samples used in testing.

The DHA results were compared for samples D and H at the start and end of testing, showing the loss of light, low-boiling compounds (Table 12), which reduced the RVP of each sample over time. The samples were stored in the cold room and were never removed from the cold room over the course of the project. It is believed that the containers may have been damaged during shipping, leading to the loss of volatile components. The RVPs of the natural gasolines were not tested prior to making the blends in this project, and it is strongly recommended that future work verify the RVP each time prior to blending.

Table 12. RVP Results for Natural Gasolines at the Start and End of the Project

Sample	Initial RVP, psi	Final RVP, psi	Notes
D	10.66	9.15	Loss of butane and pentanes confirmed by DHA
G	15.76	15.86	–
H	13.74	10.99	Loss of propane, butane, and pentanes confirmed by DHA
J	13.43	13.74	–

Two new blends of E83 were made with 200-proof ethanol and samples H and J. Table 13 shows those results (bottom two lines) and compares them to the results with the other batches of ethanol. The RVP of the E83 blend with H and the 200-proof ethanol was 6.71 psi, much closer to the predicted RVP of 6.4 psi. With ethanol batch 1 and sample H, the average RVP was 8.5 psi, though the Reddy model estimated the maximum vapor pressure would be 7.4 psi for these blends.

With sample J and 200-proof ethanol, the RVP of the blend was 8.3 psi, almost 1 psi higher than the predicted RVP of 7.4 psi. With the producer-supplied ethanol, E83 blends with sample J were about 9 psi, again much greater than the predicted RVP of 7.4 psi for these blends. The error is much greater than expected, and there does not seem to be a ready explanation for this deviation.

Table 13. Results of Natural Gasoline–BOB–Ethanol Blending for E83 for Samples H and J

Target RVP, psi	Sample / Blendstock / Ethanol	Measured RVP, psi	Predicted RVP using actual ethanol content, psi	Predicted – measured RVP, psi	Measured ethanol content, vol%	Water content, vol%	Aromatic content, vol%
7.8	H / CARBOB / Ethanol batch 1	8.34	7.6	-0.7	81.6	0.7777	2.5%
7.8	H / RBOB / Ethanol batch 1	8.26	7.6	-0.7	81.9	0.7795	2.4%
7.8	J / Ethanol batch 1	9.17	7.5	-1.6	81.6	0.7765	0.3%
7.8	J / Ethanol batch 1	9.13	7.5	-1.6	81.6	0.7894	0.3%
9.0	H / Ethanol batch 1	8.43	7.5	-0.9	81.8	0.7766	2.4%
9.0	H / Ethanol batch 1	8.52	7.6	-0.9	81.4	0.7915	2.5%
9.0	J / Ethanol batch 2	9.08	7.5	-1.6	81.9	0.7817	0.3%
9.0	J / Ethanol batch 2	8.98	7.5	-1.4	81.6	0.7883	0.3%
9.0	H / 200 proof	6.71	6.4 ^a	-0.3	82.6	0.0356	1.1%
9.0	J / 200 proof	8.26	7.4	-0.8	82.6	0.0274	0.3%

^a Predicted RVP based on 10.99 psi RVP for natural gasoline H and measured ethanol content

3.4 Reddy Model Applicability

The volume of each component in the blend was estimated to produce a finished blend with a target vapor pressure of either 7.8 psi or 9.0 psi. Once the samples were blended, the ethanol content of the blend was measured. In every sample, the ethanol content was never exactly 51 vol%, 70 vol%, or 83 vol%. To ensure that a valid comparison was made between the target RVP and the measured RVP, the measured ethanol content was used to update the predicted (or target) RVP.

Figure 2 is a graph of ethanol content versus the difference between predicted and measured RVP for the current data set and Alleman et al. (2015) data. A positive deviation (predicted – measured > 0) indicates that the model overpredicts the vapor pressure of the blend, while a negative deviation (predicted – measured < 0) means the model underpredicts the vapor pressure.

The difference between the predicted and measured ethanol content was larger than would be expected by measurement variability for RVP, ethanol, and water content. Wu and Timpe (1993) reported the influence of water content on the RVP of E10 blends. Their work found a 0.15 psi increase in the RVP of E10 as water increased from 0 to 0.2 vol%. It is not possible to extrapolate to the current work and should be considered in future work.

To illustrate the impact of RVP and ethanol measurement errors, using natural gasoline D at 83 vol% ethanol as an example, a change of 1 vol% in ethanol content would result in a change of 0.2 psi in the RVP of the fuel. The error in RVP measurement is 0.4 psi. Thus, experimental error could account for 0.6 psi difference between the measured and predicted RVP at E83. The error becomes smaller at lower ethanol contents. Thus, the differences observed between the measured and predicted RVP could not be fully explained by experimental error. This evaluation of error lead to other explanations for observed differences in RVP.

There is a tendency for greater underprediction of the RVP at higher ethanol content, though the correlation coefficient of each data point is not strong (less than 0.5). To evaluate whether the model underprediction is real and not a result of random error, the p-value for the slope was examined. For the current data, the p-value of the slope is highly significant (5.6E-8), meaning that the underprediction of the model is strongly correlated with ethanol content of the blend. Interestingly, the p-value of the slope of the 2015 data is not significant (0.119), showing that ethanol content did not have an impact on how well the model estimated the RVP of the blend. It is not clear if this was due to the smaller data set, the larger ethanol range included, or some other factor or combination of factors.

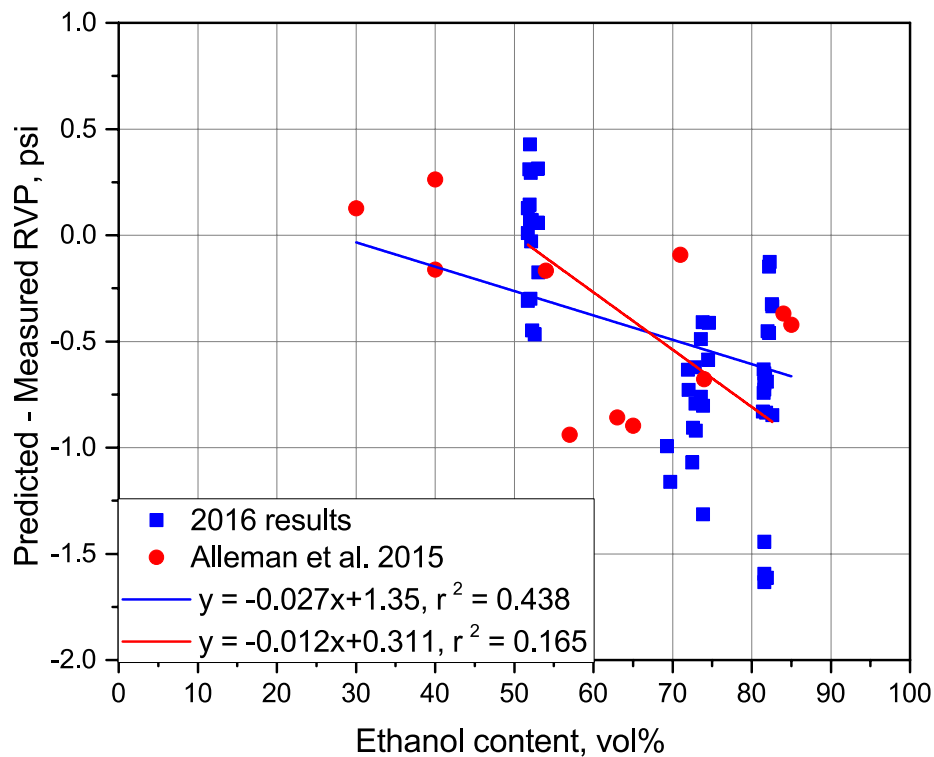


Figure 2. Ethanol content of blends versus vapor pressure

The deviation in the predicted vapor pressure, particularly for the E70 and E83 blends, was not expected when the study was designed. For this data set, deviation from Reddy's model ranged from +0.4 psi to -1.6 psi, and averaged -0.6 (Figure 3). A reexamination of the data from Alleman et al. (2015) found similar deviations, from +0.3 psi to -0.9 psi.

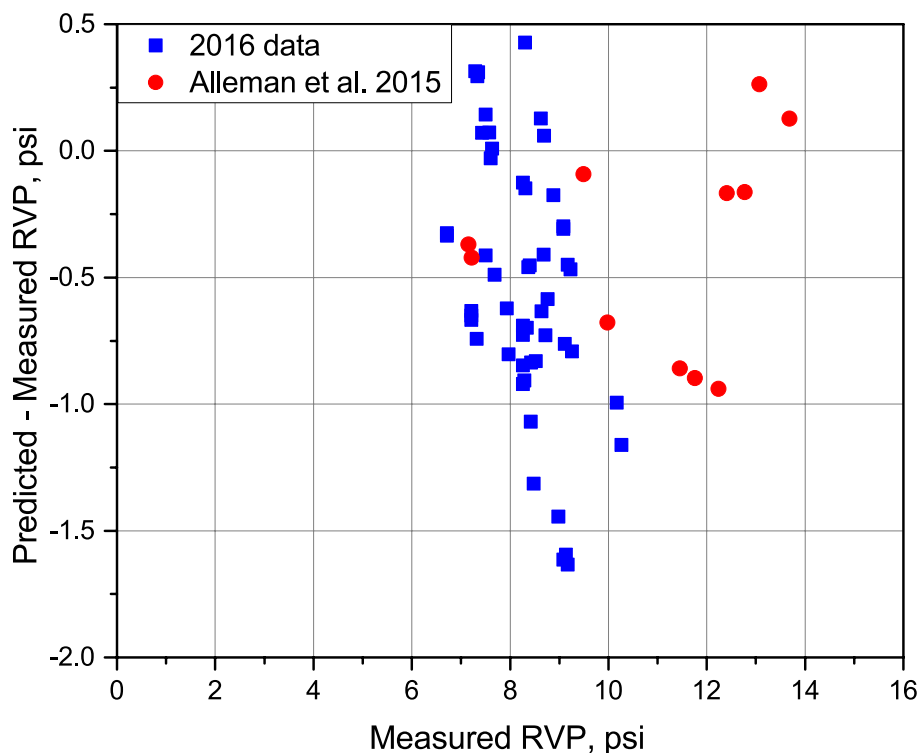


Figure 3. Difference of measured and predicted vapor pressure for natural gasoline blends

Aromatics are known to increase the solubility of polar ethanol in diesel fuel (Gerdes and Suppes 2001). Theoretically, this is because of non-covalent interaction between the aromatic ring and the polar hydroxyl group. Similarly, it might be expected that a higher aromatic content in ethanol blends might increase the attraction between ethanol and the otherwise nonpolar hydrocarbons. Using a common example, the addition of salt affects the boiling point of water (i.e., lowers its vapor pressure) by increasing the attraction of the molecules in solution, because of the highly polar nature of both of the solution components.

Analogously, we expect that if the hydrocarbon blend has a higher aromatic content it would lower the vapor pressure of the blend. The natural gasolines in this study had low aromatic contents, and thus might have resulted in a relatively higher vapor pressure than expected, which is what was observed here. To test whether aromatic content might be used to predict RVP, we compared total aromatic content of the blend with the difference between the predicted and measured RVP (Figure 4).

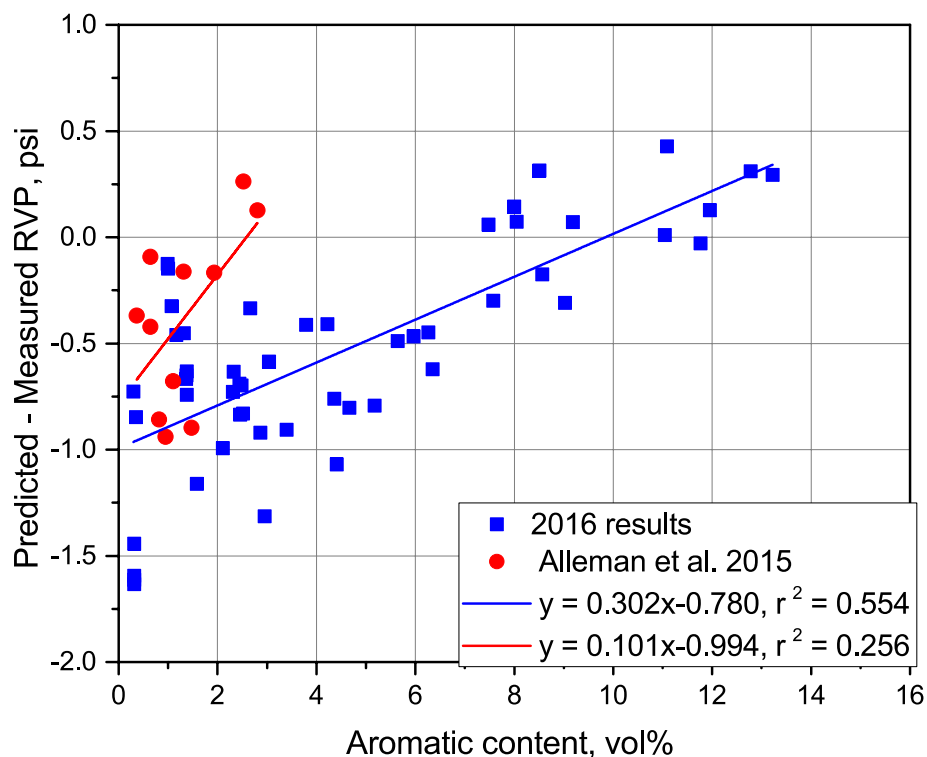


Figure 4. Impact of aromatic content of blends on difference between predicted and measured RVP

There is a reasonable correlation between aromatic content and the delta between predicted and measured RVP, and the delta is more negative as the aromatic content falls (as would be expected based on our hypothesis). While the R^2 for the 2016 data set is 0.55, it should be noted that in addition to the numerous measurements needed to predict the vapor pressure (as noted above), the aromatic content is based on the measurement of aromatics in the natural gasoline and the BOB and our estimate of the aromatic content of the denaturant. All of these measurements potentially increase the prediction error and suggest that this is a reasonably good correlation. The p-value of the slope of the regression analysis is $1.5E-10$ at the 95% confidence level, indicating the slope is significantly different from zero and that a correlation exists between aromatic content and the difference of the predicted and measured RVP.

There are several possible reasons that the E70 and E83 vapor pressure may not be predicted as accurately as the E51 vapor pressures.

- RVP testing at the start and end of the project show that two samples, D and G, lost light, volatile compounds over the course of the project, leading to a reduced RVP at the end of the project. The changes for D were smaller than those for G, though both were larger than the expected run-to-run variability for the test method of 0.4 psi. The compounds found in each sample were quite similar, and the loss was not due to a unique composition of these natural gasolines compared to the others.

- At the highest ethanol content, the impact of small changes in ethanol is more significant on the blend RVP (due to the influence of the low RVP of ethanol on the finished blends).
- For the E83 samples that were blended with ethanol batch 2, the aromatic content of the denaturant was estimated, not measured, which introduces additional error into the results.
- The aromatic content of the E70 and E83 samples is very low and the influence on RVP is more pronounced than at higher aromatic contents found in lower ethanol content samples.

Figure 5 shows the relationship between the Reddy model error and the aromatic content for each of the natural gasolines separately. At low blend aromatic contents, the model underpredicts the vapor pressure of the blend for all of the samples in this project, though the underprediction is lowest for sample G. In all cases, the p-value of the slope of the regression line is highly significant, indicating the impact of natural gasoline aromatic content on the ability of the Reddy model to predict blend RVP is real.

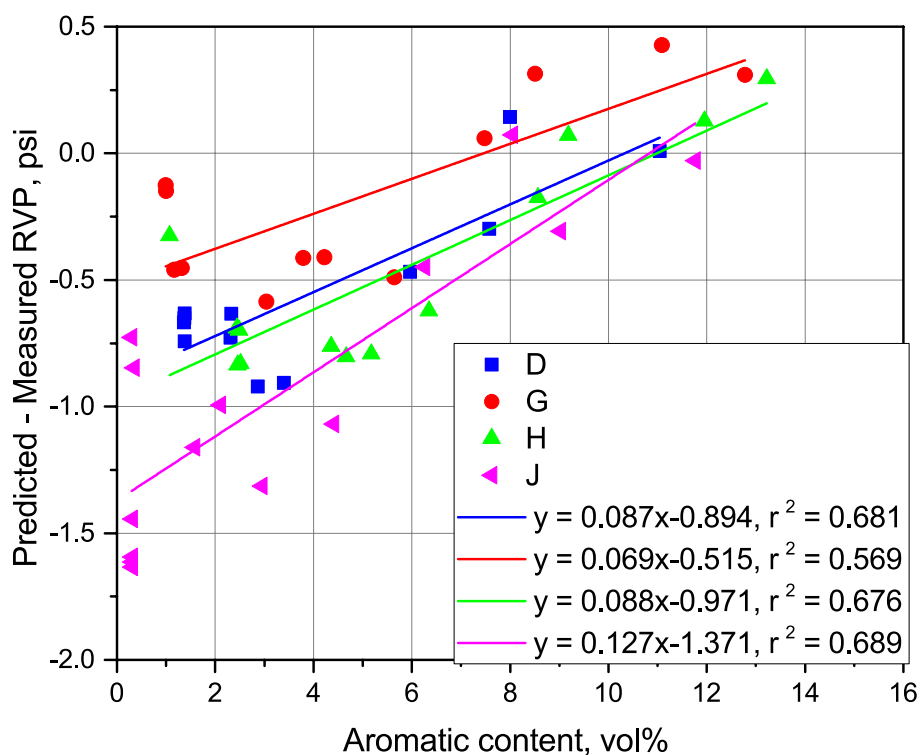


Figure 5. Influence of natural gasoline aromatic content on vapor pressure

4 Conclusions

Ten natural gasoline samples were collected from a variety of market sectors, including natural gas processing plants and ethanol providers. The natural gasolines were analyzed for a wide range of properties to fully describe this quality. Natural gasoline quality varied widely among samples, with a range of vapor pressure, sulfur, aromatic, and benzene content. All but two of the samples would meet the D8011 specification (although this specification had not been published when the samples were collected).

The project goal was to produce three component blends of E51, E70, and E83 targeting 7.8 psi and 9.0 psi for the finished blends. To produce the blends, two summertime BOBs and fuel ethanol were procured. To estimate the volumes of each component needed in the blend, the existing Reddy model (Reddy 2007) was used, assuming that the BOB and natural gasoline blended linearly and the combination could be treated as a single hydrocarbon component input to the model.

The Reddy model significantly underpredicted the blend vapor pressure by an average of 0.6 psi and by as much as 1.6 psi in this study. Generally, as ethanol content increased, the difference between the predicted RVP and the measured RVP increased. The aromatic content of the natural gasolines used were lower than that of most conventional BOBs and it is hypothesized that low aromatics lead to a higher vapor pressure in ethanol hydrocarbon blends. This is supported by a reasonably good correlation between total aromatic content in the blend and the delta between the measured and predicted RVPs ($R^2=0.55$). The significance of the slope of the regression is highly significant, providing confidence that the impact of aromatic content on the estimated RVP of these blends is real.

A complicating factor to this analysis is that two of the natural gasoline samples used in the blending lost light end components over the course of the study. The samples were stored cold throughout the project, and it is believed that container integrity may be responsible for this loss. It is highly recommended that in future work, the RVP of the natural gasolines be retested prior to blending, regardless of storage conditions, due to the light, high-volatile components found in these samples.

A second complicating factor was that three batches of ethanol were used throughout the project. The first batch was an undenatured ethanol, desired to minimize variables in the blending, such as denaturant quality and volume. The second batch of ethanol was denatured, and little information was available on the denaturant. The ethanol provider gave average properties, and an assumption was made for the study. This second batch of ethanol was used mainly for the E83 samples. To validate the results, a chemical-grade 200-proof ethanol was used to reblend two E83 samples.

The blend results from the 200-proof ethanol and sample H slightly higher than the Reddy model estimate (6.71 psi compared to an estimated 6.3 psi), while the RVP from the E83 blend with sample J was significantly higher (8.26 psi compared to an estimated 7.4 psi using the Reddy model). Sample J had the lowest aromatic content of any of the natural gasolines tested in this study. The inherently low aromatic content may contribute to the higher than estimated RVP of the blends for this sample.

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