

July 16, 1999

John DaMassa  
Planning and Technical Support Division  
California Air Resources Board  
2020 L Street  
Sacramento, CA 95814

Re: Review of Organic Gas Speciation Profiles of Exhaust and Evaporative Emissions  
from Alternate Gasoline Formulations

Dear John:

In the second phase of the speciation profile review, new headspace vapor profiles were developed using vapor-liquid equilibrium theory and liquid fuel composition profiles provided by ARB. Headspace vapor profiles were developed for 4 liquid fuels (gasoline with MTBE @ 2 wt% oxygen, gasoline with ethanol @ 2 wt% oxygen, gasoline with ethanol @ 3.5 wt% oxygen, and gasoline without oxygenates).

The theoretical calculations of headspace vapor composition presented here were made because ARB staff had concerns about the applicability and consistency of available vehicle test data used to characterize speciation of diurnal evaporative emissions, especially for ethanol-containing gasoline blends. However, it should be noted that while headspace vapor composition can be used to represent the speciation of some vapor displacement emissions that occur during vehicle refueling (Furey and Nagel, 1986), the presence of control equipment such as activated carbon canisters can affect the speciation of diurnal evaporative emissions (Urbanic et al., 1989). Therefore, calculated headspace vapor composition profiles developed here may not represent the composition of diurnal evaporative emissions. Furthermore, while the vapor-liquid equilibrium theory and methods used here have been verified for pure hydrocarbon and hydrocarbon-MTBE mixtures, measured headspace vapor composition profiles for ethanol-containing gasolines were not available from ARB at the time this report was prepared. Predicted headspace vapor composition profiles for the ethanol-containing gasolines should be evaluated using measured values before these profiles can be considered for use.

## METHODS

Liquid fuel profiles were sent by Paul Allen via E-mail on June 8, together with profiles for other exhaust and evaporative emission categories. On July 8, I was advised of the following revisions to profile 650 (liquid fuel profile for gasoline without oxygenates): benzene, 0.799 wt%; 1-butene, 0.008 wt%; n-butane, 0.807 wt%; isobutane, 0.136 wt%. These resulted from a change in ARB's recipe for predicting the composition of gasoline without oxygenates: the recipe step of converting 80% of butanes to 1-butene was deleted. On July 15, I was advised that one further revision had been made to the fuel profiles: benzene had been set uniformly at 1.0 wt% in the liquid phase for all 4 fuels. I did not renormalize the liquid fuel profiles after these changes; the revised sum of species was within  $100.0 \pm 0.1$  wt% in all cases.

Starting from the composition specified for liquid fuel, vapor-liquid equilibrium theory was used to predict headspace vapor composition. This procedure has been described and verified by comparing predicted and measured headspace vapor profiles (Furey and Nagel, 1986; Kirchstetter et al., 1999). These studies both caution that assuming ideal solution behavior is not appropriate for gasoline containing ethanol.

For ideal solutions, the partial pressure ( $P_i$ ) of a species in the headspace above the liquid is given by Raoult's law:

$$P_i = x_i P_{i,sat}$$

where  $x_i$  is the mole fraction of the species in the liquid phase, and  $P_{i,sat}$  is the saturation vapor pressure of the pure liquid. To predict vapor pressures for non-ideal solutions, activity coefficients  $g_i$  must be included:

$$P_i = g_i x_i P_{i,sat}$$

Tables II and III of Bennett et al. (1993) present measured vapor and liquid-phase mole fractions for various equilibrium mixtures containing MTBE or ethanol plus a paraffin (2,2,4-trimethylpentane), an olefin (1-heptene), a naphthene (methylcyclohexane), and an aromatic (toluene). Activity coefficients were back-calculated from measured liquid ( $x_i$ ) and vapor ( $y_i$ ) mole fractions and measured vapor pressure ( $P_{tot}$ ):

$$g_i = \frac{y_i P_{tot}}{x_i P_{i,sat}}$$

Pure liquid vapor pressures ( $P_{i,sat}$ ) were calculated for the conditions of each experiment for each species using the Wagner equation (see Appendix A).

Activity coefficients for MTBE and ethanol are presented in Figures 1 and 2 as a function of the mole fraction of oxygenate in the liquid phase. Figure 1 shows that MTBE's behavior in solution with a mixture of hydrocarbons is closely approximated by Raoult's law (i.e.,  $\gamma_{\text{MTBE}} = 1$ ), whereas the partial pressure of ethanol in the headspace exceeds the Raoult's law prediction by factors of 2-5 for ethanol mole fractions of 10-20% in the liquid (this range corresponds approximately to 5-10 vol% ethanol in fuel). Figures 1 and 2 also indicate that the effect of temperature on activity coefficients is small over the range from 25 to 60 C.

Activity coefficients listed in Table 1 were used to estimate headspace vapor composition for each of the 4 liquid fuel profiles provided by ARB. Separate activity coefficients were specified for each fuel; near-ideal solution behavior was expected for gasoline without oxygenates and gasoline with MTBE. A small increment in aromatics ( $\gamma=1.2$ ) in headspace vapors for these two fuels was suggested by data of Bennett et al. (1993) for toluene. Larger departures from ideal solution behavior were specified for the gasoline-ethanol blends, as shown in Table 1.

**Table 1:** Activity Coefficients Used to Estimate Headspace Vapor Composition for Alternate Liquid Fuel Formulations

	Fuel 419	Fuel 650	Fuel 660	Fuel 670
Compound Class	MTBE @ 2%	No oxygenates	Ethanol @ 2%	Ethanol @ 3.5%
Paraffins	1.1	1.0	1.6	1.8
Naphthenes	1.1	1.0	1.6	1.7
Olefins	1.1	1.0	1.5	1.6
Aromatics	1.2	1.2	1.6	1.7
MTBE	1.0	N/A	N/A	N/A
Alcohols	10. <sup>a</sup>	10. <sup>a</sup>	4.5	2.8

<sup>a</sup>Highly non-ideal behavior is expected from Figure 2 for small amounts of alcohols that may be present in fuels that are nominally "without ethanol".

## RESULTS

A summary of the most abundant species in gasoline headspace vapors is presented in Table 2. Isopentane accounts for about a third of headspace vapor mass, except for gasoline without oxygenates where it is nearly half of the total. Ethanol or MTBE also are abundant in the headspace when present in the liquid fuels. The other most abundant species are alkanes with low molecular weights and high vapor pressures: n-butane, n-pentane, and 2-methylpentane.

The 23 species listed in Table 2 together account for 90% or more of the total headspace vapors for each fuel. Full headspace vapor speciation profiles are provided in Appendix B.

## DISCUSSION

In each of the oxygenated fuels, the oxygenate accounts for a significant fraction of headspace vapor mass. MTBE comprises ~15 wt% of headspace vapors when added at 2 wt% oxygen in liquid fuel, and ethanol is in the range 9-10 wt% of headspace vapors for both fuels containing ethanol. Ethanol in the liquid phase almost doubles from 5.75 to 10.1 wt% between the two fuels containing ethanol, but its fraction in the headspace hardly changes. This non-linear relationship between fuel and headspace vapor composition is due to the decrease in ethanol's activity coefficient as the ethanol increases in the liquid, as shown in Figure 2. The relationship between the weight fraction of ethanol in the liquid phase and in headspace vapors should be confirmed in the laboratory by measuring headspace vapor composition for real gasoline samples with different ethanol contents.

Olefins are an important part of the headspace vapor composition profiles because they are highly reactive in the atmosphere compared to other compounds such as alkanes, MTBE, and ethanol (Carter, 1994). The list of the most abundant species in headspace vapors (Table 2) includes four C<sub>5</sub> olefins: 2-methyl-2-butene, trans-2-pentene, 2-methyl-1-butene, and cis-2-pentene. Although none of these species are abundant in liquid fuels (all are <0.5% except for 2-methyl-2-butene in gasoline with MTBE), their high vapor pressures lead to increased amounts of these compounds in headspace vapors. Laboratory studies of fuel composition and evaporative emissions should pay special attention to identifying and quantifying olefins and diolefins in the C<sub>4</sub>-C<sub>6</sub> range.

In addition to impacts on ozone, an important part of the air quality assessment for the alternate fuels will be consideration of air toxics including benzene. Table 2 indicates increased benzene levels in headspace vapors for the ethanol-containing fuels. The predictions of benzene in the headspace vapors of ethanol-containing gasoline blends should be verified against laboratory measurements of headspace vapor composition.

In addition to calculating headspace vapor composition, the total vapor pressure  $P_{tot}$  for each gasoline at 100 F (38 C) was estimated as

$$P_{tot} = \sum_i P_i$$

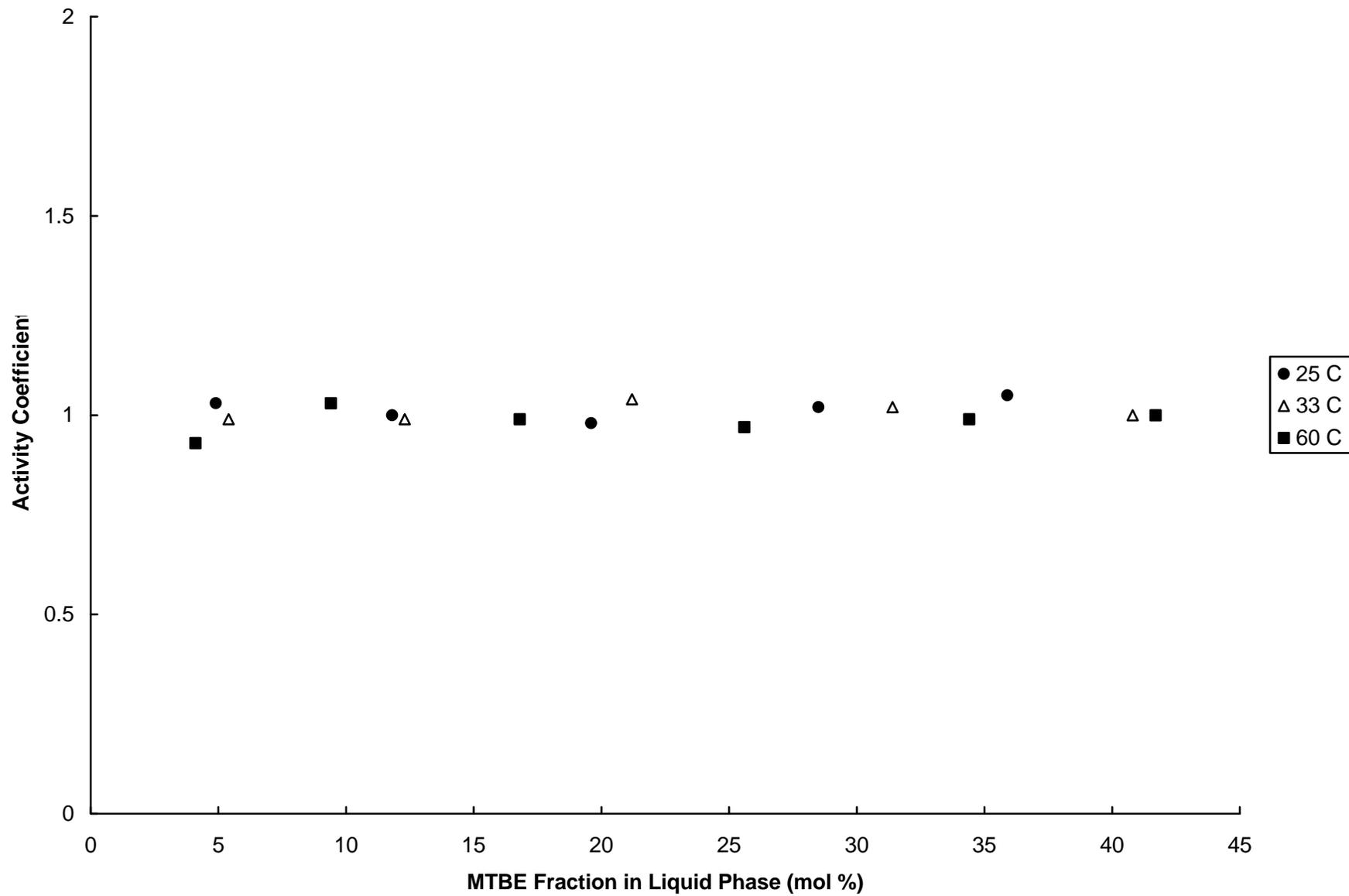
where  $P_i$  is the partial pressure of species  $i$  in headspace vapors calculated as described above.

**Table 2:** Comparison of Most Abundant Species in Gasoline Headspace Vapors

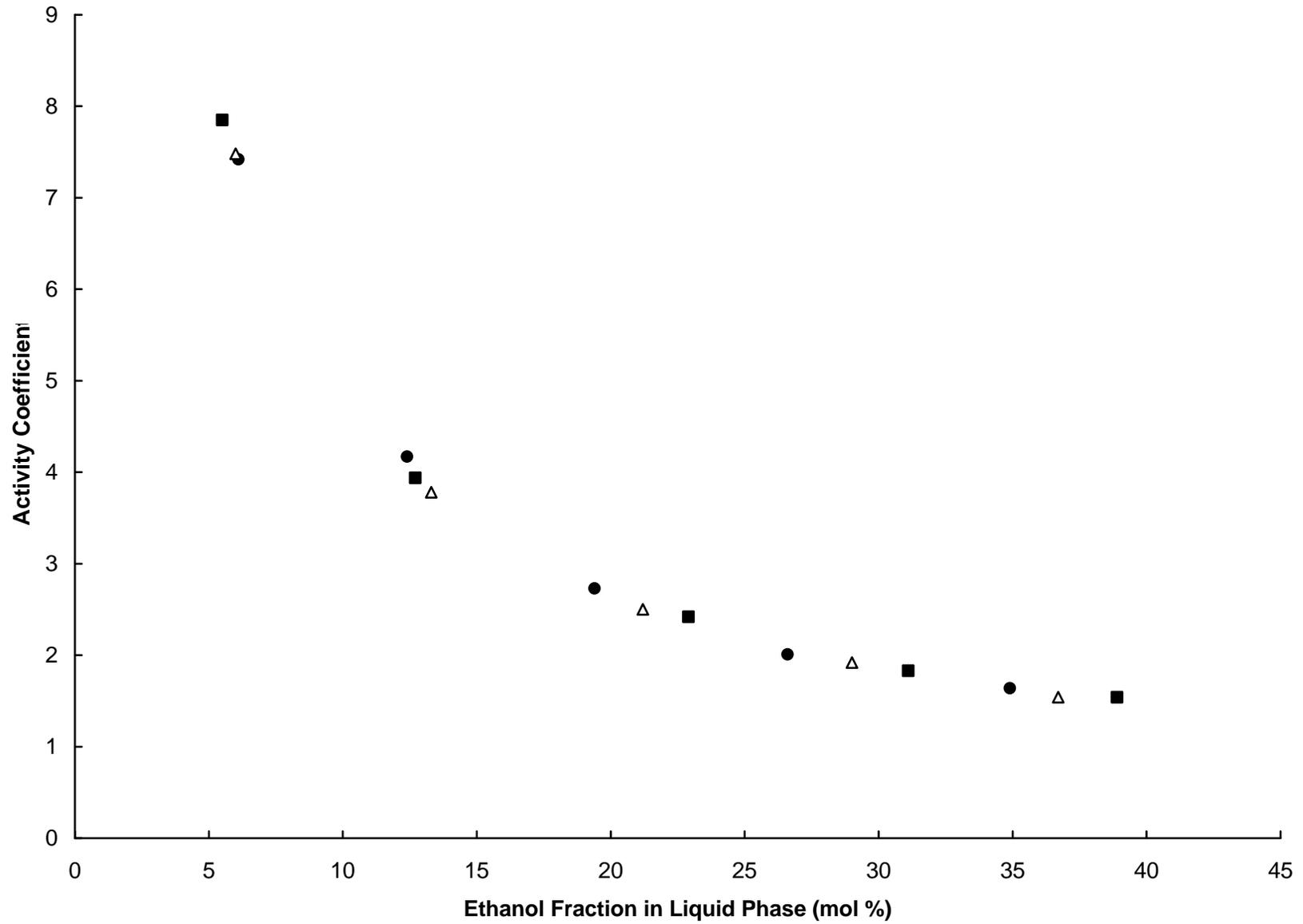
Species Name	MTBE 2%		ETOH 2%		ETOH 3.5%		NO OXY	
	weight percent in head space	rank						
isopentane	36.5	1	32.0	1	32.2	1	46.8	1
ethyl alcohol	0.0	n/a	9.3	3	9.6	3	0.0	n/a
methyl t-butyl ether (MTBE)	15.2	2	0.0	n/a	0.0	n/a	0.0	n/a
n-butane	9.5	3	10.3	2	10.4	2	7.4	2
n-pentane	5.1	4	4.5	4	4.5	4	6.6	3
2-methylpentane	5.1	5	4.5	5	4.5	5	6.5	4
3-methylpentane	2.5	6	2.2	12	2.2	12	3.3	5
isobutane	2.2	7	2.9	7	2.9	7	1.7	9
2,3-dimethylbutane	1.8	8	1.5	13	1.6	13	2.3	7
2,2,4-trimethylpentane	1.7	9	4.1	6	4.1	6	2.6	6
2-methyl-2-butene	1.6	10	1.2	15	1.2	15	1.2	15
toluene	1.4	11	1.3	14	1.2	14	0.9	17
methylcyclopentane	1.3	12	1.1	16	1.0	16	1.6	12
2,3-dimethylpentane	1.2	13	2.9	8	2.9	8	1.9	8
trans-2-pentene	1.1	14	0.9	18	0.8	18	0.9	16
3-methylhexane	1.1	15	2.7	9	2.7	9	1.7	10
n-hexane	1.1	16	0.9	17	0.9	17	1.4	14
2-methylhexane	1.1	17	2.6	10	2.6	10	1.7	11
2,4-dimethylpentane	1.0	18	2.5	11	2.5	11	1.6	13
2-methyl-1-butene	0.77	19	0.59	22	0.57	22	0.60	19
benzene	0.64	20	0.80	19	0.80	19	0.69	18
cis-2-pentene	0.60	21	0.47	24	0.45	25	0.47	21
n-heptane	0.48	22	0.63	20	0.63	20	0.38	23
sum of above species	93		90		90		92	

Calculated vapor pressures for each fuel are 7.6 psi for gasoline with MTBE, 8.3 and 8.5 psi for gasoline with ethanol at 2 and 3.5 wt% oxygen, and 7.1 psi for gasoline without oxygenates. Note that predictions of absolute vapor pressure may be less accurate than predictions of the relative abundance of species in headspace vapors. Furthermore, these calculations do not reproduce exactly the conditions of the Reid Vapor Pressure test used to certify fuels. Nevertheless, the detailed liquid fuel formulations provided by ARB, especially those for gasolines with ethanol, may not be representative of fuels that comply with California's summertime RVP limits.

**Figure 1:** Activity Coefficient for MTBE vs. MTBE Content in Liquid Phase



**Figure 2:** Activity Coefficient for Ethanol vs. Ethanol Content in Liquid Phase



## REFERENCES

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## **ACKNOWLEDGMENTS**

I am grateful to Shannon Coulter-Burke, a student at UC Berkeley, for assisting me with the calculation of headspace vapor composition profiles.

Sincerely,

Robert Harley  
Associate Professor

## APPENDIX A: FURTHER DESCRIPTION OF METHODOLOGY USED TO PREDICT HEADSPACE VAPOR COMPOSITION

For each of the pure compounds present in gasoline, the saturation pressure at 100 F (T=311 K) was calculated using the Wagner equation:

$$\ln P_r = \frac{at + bt^{1.5} + ct^3 + dt^6}{1 - t}$$

where a, b, c, and d are constants specific to each species and  $\tau=1- T_r$ .  $P_r$  and  $T_r$  are the reduced pressure and temperature:  $P_r = P_{i,\text{sat}}/P_c$  and  $T_r = T/T_c$  where  $P_{i,\text{sat}}$  is the saturation vapor pressure (atm), T is the temperature (K), and  $P_c$  and  $T_c$  are the critical pressure and temperature of pure species i. Values of all parameters needed in the Wagner equation are tabulated in Appendix 1 of Reid et al. (1987). For some compounds, the vapor pressure was estimated using alternate equations such as Antoine or Frost-Kalkwarf-Thodos, again using data from Appendix 1 of Reid et al. (1987).

The liquid fuel profiles that were provided specify composition in terms of weight fractions ( $w_i$ ) instead of mole fractions ( $x_i$ ). The following formula was used to convert the liquid profiles from mass to molar basis, using the molecular weights  $M_i$  for each species:

$$x_i = \frac{w_i / M_i}{\sum_i w_i / M_i}$$

Likewise the final headspace vapor composition profiles were converted from mole fraction ( $y_i$ ) to weight fraction ( $w_i$ ) using the following formula:

$$w_i = \frac{y_i M_i}{\sum_i y_i M_i}$$

## Appendix B: Full Headspace Vapor Speciation Profiles

SAROAD	Species Name	MTBE 2%	ETOH 2%	ETOH 3.5%	NO OXY
		wt %	wt %	wt %	wt %
Number	Species Name	headspace	headspace	headspace	headspace
45201	benzene	0.64	0.80	0.80	0.69
45202	toluene	1.36	1.31	1.24	0.86
45203	ethylbenzene	0.16	0.15	0.14	0.10
45209	n-propylbenzene	0.01	0.01	0.01	0.01
98043	isopropylbenzene (cumene)	0.00	0.00	0.00	0.00
91098	n-butylbenzene	0.00	0.00	0.00	0.00
98047	isobutylbenzene	0.00	0.00	0.00	0.00
45216	sec-butylbenzene	0.00	0.00	0.00	0.00
91111	s-pentylbenzene	0.00	0.00	0.00	0.00
91121	n-hexylbenzene	0.00	0.00	0.00	0.00
45205	m-xylene	0.23	0.22	0.21	0.14
45204	o-xylene	0.11	0.11	0.10	0.07
45206	p-xylene	0.12	0.12	0.11	0.08
99912	1-methyl-3-ethylbenzene	0.04	0.03	0.03	0.02
99914	1-methyl-4-ethylbenzene	0.01	0.01	0.01	0.01
99915	1-methyl-2-ethylbenzene	0.01	0.01	0.01	0.01
98152	1-methyl-3n-propylbenzene	0.00	0.00	0.00	0.00
98182	1-methyl-4n-propylbenzene	0.00	0.00	0.00	0.00
45113	1,3-diethylbenzene (meta)	0.00	0.00	0.00	0.00
98153	1-methyl-3-isopropylbenzene	0.00	0.00	0.00	0.00
91096	1-methyl-2-isopropylbenzene	0.00	0.00	0.00	0.00
98154	1,2-diethylbenzene (ortho)	0.00	0.00	0.00	0.00
91094	1-methyl-4-isopropylbenzene	0.00	0.00	0.00	0.00
98179	1-ethyl-2n-propylbenzene	0.00	0.00	0.00	0.00
45245	c11 dialkyl benzenes	0.00	0.00	0.00	0.00
91100	1-methyl-4-t-butylbenzene	0.00	0.00	0.00	0.00
45237	1,3-dipropylbenzene	0.00	0.00	0.00	0.00
91113	1,2-isodipropylbenzene	0.00	0.00	0.00	0.00
91120	1-methyl-4-n-pentylbenzene	0.00	0.00	0.00	0.00
91116	1,3-n-dipropylbenzene	0.00	0.00	0.00	0.00
45247	c12 dialkyl benzenes	0.00	0.00	0.00	0.00
45208	1,2,4-trimethylbenzene	0.03	0.03	0.03	0.02
45207	1,3,5-trimethylbenzene	0.02	0.02	0.01	0.01
45225	1,2,3-trimethylbenzene	0.00	0.00	0.00	0.00
45252	1,2-dimethyl-4-ethylbenzene	0.00	0.00	0.00	0.00
45257	1,3-dimethyl-5-ethylbenzene	0.00	0.00	0.00	0.00
45250	1,4-dimethyl-2-ethylbenzene	0.00	0.00	0.00	0.00
45251	1,3-dimethyl-4-ethylbenzene	0.00	0.00	0.00	0.00
45254	1,2-dimethyl-3-ethylbenzene	0.00	0.00	0.00	0.00
45253	1,3-dimethyl-2-ethylbenzene	0.00	0.00	0.00	0.00
91117	1,3,5-triethylbenzene	0.00	0.00	0.00	0.00
91119	1,2,4-triethylbenzene	0.00	0.00	0.00	0.00
98044	indan	0.00	0.00	0.00	0.00
98046	naphthalene	0.00	0.00	0.00	0.00
91104	1,2,3,5-tetramethylbenzene	0.00	0.00	0.00	0.00
91108	2-methylindan	0.00	0.00	0.00	0.00
91106	5-methylindan	0.00	0.00	0.00	0.00
91103	1,2,4,5-tetramethylbenzene	0.00	0.00	0.00	0.00
91107	4-methylindan	0.00	0.00	0.00	0.00
46751	dihydronaphthalene	0.00	0.00	0.00	0.00
91123	2-methylnaphthalene	0.00	0.00	0.00	0.00
91124	1-methylnaphthalene	0.00	0.00	0.00	0.00
91122	pentamethylbenzene	0.00	0.00	0.00	0.00
43242	cyclopentane	0.25	0.22	0.21	0.32

## Appendix B: Full Headspace Vapor Speciation Profiles

43262	methylcyclopentane	1.26	1.10	1.05	1.61
43248	cyclohexane	0.13	0.11	0.11	0.17
43261	methylcyclohexane	0.22	0.53	0.50	0.34
91018	1-c-3-dimethylcyclopentane	0.19	0.46	0.43	0.29
91019	1-t-3-dimethylcyclopentane	0.17	0.42	0.40	0.27
91021	1-t-2-dimethylcyclopentane	0.14	0.35	0.33	0.22
98057	ethylcyclopentane	0.05	0.13	0.12	0.08
91029	1-c-2-dimethylcyclopentane	0.05	0.12	0.12	0.08
90064	dimethylcyclopentane	0.03	0.07	0.06	0.04
91038	1c,2t,3-trimethylcyclopentane	0.03	0.07	0.07	0.05
43116	c8 cycloparaffins	0.02	0.05	0.05	0.03
91031	1c,2t,4-trimethylcyclopentane	0.04	0.09	0.08	0.06
91032	1t,2c,3-trimethylcyclopentane	0.01	0.02	0.02	0.01
91047	t-1,2-dimethylcyclohexane	0.01	0.02	0.02	0.01
91050	1c,2c,3-trimethylcyclopentane	0.01	0.02	0.02	0.01
98180	cis-1,3-dimethylcyclohexane	0.01	0.02	0.02	0.02
98181	trans-1,4-dimethylcyclohexane	0.01	0.03	0.02	0.02
91045	t-2-ethylmethylcyclopentane	0.01	0.01	0.01	0.01
90116	propylcyclopentane	0.00	0.01	0.01	0.01
91055	c-1,2-dimethylcyclohexane	0.00	0.01	0.01	0.00
91033	1,1,2-trimethylcyclopentane	0.00	0.01	0.01	0.01
98059	trans-1,3-dimethylcyclohexane	0.00	0.01	0.01	0.00
91041	1,1-dimethylcyclohexane	0.00	0.00	0.00	0.00
91046	1,1-methylethylcyclopentane	0.00	0.00	0.00	0.00
91077	i-butylcyclopentane	0.00	0.01	0.01	0.01
91057	1,1,4-trimethylcyclohexane	0.00	0.01	0.01	0.00
91061	c-1,c-3,5-trimethylcyclohexane	0.00	0.00	0.00	0.00
91081	1,1-methylethylcyclohexane	0.00	0.00	0.00	0.00
91066	c1,t2,t4-trimethylcyclohexane	0.00	0.00	0.00	0.00
91085	n-butylcyclopentane	0.00	0.00	0.00	0.00
90120	propylcyclohexane	0.00	0.00	0.00	0.00
91064	1,1,3-trimethylcyclohexane	0.00	0.00	0.00	0.00
91074	1,1,2-trimethylcyclohexane	0.00	0.00	0.00	0.00
98060	trimethylcyclohexane	0.00	0.00	0.00	0.00
90101	butylcyclohexane	0.00	0.00	0.00	0.00
43213	1-butene	0.11	0.09	0.09	0.09
43225	2-methyl-1-butene	0.77	0.59	0.57	0.60
43224	1-pentene	0.42	0.32	0.31	0.33
43223	3-methyl-1-butene	0.10	0.07	0.07	0.07
98040	2-methyl-1-pentene	0.12	0.09	0.09	0.09
43245	1-hexene	0.07	0.05	0.05	0.05
98135	4-methyl-1-pentene	0.03	0.03	0.02	0.03
43211	3-methyl-1-pentene	0.02	0.02	0.02	0.02
43234	2,3-dimethyl-1-butene	0.01	0.01	0.01	0.01
91000	3,3-dimethyl-1-pentene	0.06	0.05	0.05	0.05
91008	4-methyl-1-hexene	0.01	0.01	0.01	0.01
90063	2,4-dimethyl-1-pentene	0.00	0.00	0.00	0.00
91005	5-methyl-1-hexene	0.00	0.00	0.00	0.00
43267	1-nonene	0.00	0.00	0.00	0.00
91067	2-methyl-1-octene	0.00	0.00	0.00	0.00
43216	trans-2-butene	0.09	0.07	0.07	0.07
43217	cis-2-butene	0.08	0.06	0.06	0.07
43228	2-methyl-2-butene	1.59	1.23	1.17	1.24
43226	trans-2-pentene	1.12	0.87	0.83	0.88
43227	cis-2-pentene	0.60	0.47	0.45	0.47
43292	cyclopentene	0.15	0.12	0.11	0.12
98004	2-methyl-2-pentene	0.18	0.14	0.13	0.14

Appendix B: Full Headspace Vapor Speciation Profiles

92000	1-methylcyclopentene	0.16	0.12	0.12	0.12
98034	trans-2-hexene	0.16	0.12	0.12	0.12
43272	3-methylcyclopentene	0.10	0.08	0.08	0.08
98035	cis-2-hexene	0.08	0.06	0.06	0.06
98136	trans-3-hexene	0.08	0.06	0.06	0.07
43293	4-methyl-trans-2-pentene	0.10	0.08	0.07	0.08
98163	3-methyl-cis-2-pentene	0.04	0.03	0.03	0.03
43273	cyclohexene	0.03	0.02	0.02	0.02
98003	cis-3-hexene	0.03	0.02	0.02	0.02
90029	3-methyl-cis-2-hexene	0.06	0.04	0.04	0.04
91027	3-methyl-trans-2-hexene	0.05	0.04	0.04	0.04
98006	trans-3-heptene	0.05	0.04	0.03	0.04
91001	4,4-dimethyl-2-pentene	0.02	0.02	0.02	0.02
91026	trans-2-heptene	0.02	0.02	0.02	0.02
91028	cis-2-heptene	0.02	0.02	0.02	0.02
90031	4-methyl-trans-2-hexene	0.02	0.01	0.01	0.01
90032	3-methyl-trans-3-hexene	0.02	0.01	0.01	0.01
91024	3-methyl-cis-3-hexene	0.01	0.01	0.01	0.01
91006	2-methyl-trans-3-hexene	0.01	0.01	0.01	0.01
98007	3-ethyl-2-pentene	0.01	0.01	0.01	0.01
91011	3,4-dimethyl-2-pentene	0.01	0.01	0.01	0.01
91017	5-methyl-cis-2-hexene	0.00	0.00	0.00	0.00
43263	trans-2-octene	0.00	0.00	0.00	0.00
43250	trans-4-octene	0.00	0.00	0.00	0.00
43266	cis-2-octene	0.00	0.00	0.00	0.00
91084	cis-3-nonene	0.00	0.00	0.00	0.00
91080	trans-3-nonene	0.00	0.00	0.00	0.00
91092	2,3-dimethyl-2-octene	0.00	0.00	0.00	0.00
90100	trans-1,3-pentadiene	0.07	0.05	0.05	0.05
43243	isoprene	0.03	0.02	0.02	0.02
90026	1,3-cyclopentadiene	0.02	0.02	0.02	0.02
99999	unidentified	0.00	0.00	0.00	0.00
43301	methyl alcohol	0.09	0.04	0.02	0.08
43302	ethyl alcohol	0.00	9.35	9.56	0.00
43303	n-propyl alcohol	0.03	0.01	0.01	0.03
43378	methyl t-butyl ether (MTBE)	15.20	0.00	0.00	0.00
43212	n-butane	9.49	10.31	10.36	7.42
43220	n-pentane	5.11	4.48	4.50	6.54
43231	n-hexane	1.08	0.94	0.95	1.38
43232	n-heptane	0.48	0.63	0.63	0.38
43233	n-octane	0.06	0.08	0.08	0.05
43235	n-nonane	0.01	0.01	0.01	0.00
43238	n-decane	0.00	0.00	0.00	0.00
43241	n-undecane	0.00	0.00	0.00	0.00
43255	n-dodecane	0.00	0.00	0.00	0.00
43214	isobutane	2.23	2.92	2.92	1.74
98132	isopentane	36.51	32.03	32.17	46.78
43229	2-methylpentane	5.10	4.48	4.50	6.54
43230	3-methylpentane	2.54	2.23	2.24	3.26
43295	3-methylhexane	1.10	2.67	2.68	1.72
43275	2-methylhexane	1.08	2.61	2.62	1.67
43300	3-ethylpentane	0.10	0.25	0.25	0.16
43298	3-methylheptane	0.10	0.24	0.24	0.15
98140	2-methylheptane	0.10	0.23	0.23	0.15
43297	4-methylheptane	0.04	0.10	0.10	0.06
91039	3-ethylhexane	0.01	0.02	0.02	0.01
98172	3-methyloctane	0.01	0.03	0.03	0.02

Appendix B: Full Headspace Vapor Speciation Profiles

98146	2-methyloctane	0.01	0.02	0.02	0.02
98173	4-methyloctane	0.01	0.02	0.02	0.01
91071	3-ethylheptane	0.00	0.01	0.01	0.00
90047	2-methylnonane	0.00	0.00	0.00	0.00
91090	3-methylnonane	0.00	0.00	0.00	0.00
91088	5-methylnonane	0.00	0.00	0.00	0.00
91089	3-ethyloctane	0.00	0.00	0.00	0.00
91097	3-ethylnonane	0.00	0.00	0.00	0.00
98130	2,2-dimethylpropane	0.07	0.06	0.06	0.09
98001	2,3-dimethylbutane	1.76	1.55	1.55	2.26
43291	2,2-dimethylbutane	0.43	0.38	0.38	0.55
43274	2,3-dimethylpentane	1.19	2.89	2.90	1.85
43271	2,4-dimethylpentane	1.03	2.49	2.51	1.60
90040	3,3-dimethylpentane	0.10	0.25	0.25	0.16
90042	2,2-dimethylpentane	0.01	0.01	0.01	0.01
43277	2,4-dimethylhexane	0.17	0.41	0.41	0.26
43278	2,5-dimethylhexane	0.12	0.30	0.30	0.19
98139	2,3-dimethylhexane	0.09	0.23	0.23	0.15
98138	2,2-dimethylhexane	0.03	0.08	0.08	0.05
91036	3-methyl-3-ethylpentane	0.01	0.04	0.04	0.02
98150	3,4-dimethylhexane	0.01	0.03	0.03	0.02
91034	2-methyl-3-ethylpentane	0.01	0.02	0.02	0.01
98171	3,3-dimethylhexane	0.01	0.02	0.02	0.01
98143	2,5-dimethylheptane	0.01	0.03	0.03	0.02
98145	2,3-dimethylheptane	0.01	0.01	0.01	0.01
91063	3,3-dimethylheptane	0.00	0.01	0.01	0.01
91069	3,4-dimethylheptane	0.00	0.01	0.01	0.01
91060	4,4-dimethylheptane	0.00	0.01	0.01	0.00
98144	3,5-dimethylheptane	0.00	0.00	0.00	0.00
98142	2,4-dimethylheptane	0.00	0.00	0.00	0.00
98176	2,5-dimethyloctane	0.00	0.00	0.00	0.00
98184	3,3-dimethyloctane	0.00	0.00	0.00	0.00
98149	2,4-dimethyloctane	0.00	0.00	0.00	0.00
98177	2,6-dimethyloctane	0.00	0.00	0.00	0.00
91086	3,6-dimethyloctane	0.00	0.00	0.00	0.00
98175	2,2-dimethyloctane	0.00	0.00	0.00	0.00
43160	2,2,3-trimethylbutane	0.02	0.06	0.06	0.04
43276	2,2,4-trimethylpentane	1.70	4.11	4.13	2.64
43279	2,3,4-trimethylpentane	0.25	0.61	0.62	0.39
43280	2,3,3-trimethylpentane	0.18	0.45	0.45	0.29
43296	2,2,3-trimethylpentane	0.03	0.07	0.07	0.04
98033	2,2,5-trimethylhexane	0.08	0.19	0.19	0.12
91053	2,3,4-trimethylhexane	0.01	0.02	0.02	0.02
98141	2,3,5-trimethylhexane	0.01	0.02	0.02	0.01
91059	2,2,3,trimethylhexane	0.01	0.01	0.01	0.01
45222	2,2,4-trimethylhexane	0.00	0.00	0.01	0.00
45223	2,4,4-trimethylhexane	0.00	0.00	0.00	0.00