Organic Gas Speciation Profile
for Headspace Vapor of E10 Summer Gasoline Fuel (OG691)

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1 Introduction

The current CARB organic gas speciation profiles for headspace vapor of gasoline is OG661 (Headspace vapors 1996 SSD ethanol 2.0% oxygen, MTBE phased out) [1]. This profile was generated by applying vapor-liquid equilibrium theory to liquid gasoline fuel profile OG660 (Liquid gasoline 1996 SSD ethanol 2.0% oxygen, MTBE phased out) in 1999 [2]. It is widely used for categories of on-road gasoline vehicle resting loss, off-road equipment gasoline evaporative, and a variety of losses from petroleum marketing and petroleum storage. Based on the 2009 Almanac projection for year 2010, the statewide annual average TOG emissions of these categories are 220.63 tons/day, 3.88% of the grand total TOG emissions.

It is known that all commercial gasoline fuels in California contain 10%wt ethanol (i.e. E10, or 3.5%wt oxygen) starting from 2010. However, the current gasoline headspace vapor profile OG661 was made specifically for gasoline containing 6%wt ethanol (i.e. E6, or 2.0%wt oxygen), and it is not appropriate to be used for E10 fuel. Therefore, an equilibrium headspace vapor profile of E10 fuel is created based on the newly developed E10 liquid gasoline profile OG690 in this work. The new gasoline vapor profile is OG 691, and it will be used to replace OG661 for the related emission categories for 2010 and later years.

2 Methodology

Because there is no speciation test data available for E10 fuel headspace vapor, the new profile OG691 was predicted using vapor-liquid equilibrium theory. The methodology of the profile development is similar to the one used to develop OG661 [2].

Partial pressures p_i of organic species *i* present in gasoline headspace vapors were predicted using Equation 1:

$$\boldsymbol{p_i = \gamma_i x_i p_i^o} \tag{1}$$

where γ_i is the liquid-phase activity coefficient of species *i*, x_i is the mole fraction of species *i* in liquid fuel, and p_i^o is the vapor pressure of species *i* in pure liquid form. Activity coefficients γ_i for E10 fuel were listed in Harley et al [3]. Mole fractions x_i were converted from the weight fractions of the liquid fuel profile by dividing the molecular weights for each compound. Pure liquid vapor pressures were estimated as a function of temperature using the Wagner Equation (Equation 2) [4]:

$$\ln p_r^o = \frac{a\tau + b\tau^{1.5} + c\tau^{2.5} + d\tau^5}{T_r} \tag{2}$$

where $p_r^o = p_i^o / p_c$ is reduced vapor pressure, $T_r = T/T_c$ is reduced temperature, p_c and T_c are critical point pressure and temperature, and $\tau = 1 - T_r$. Values of p_c, T_c, a, b, c, and d for many of the species were obtained from Appendix A of Poling et al. [4]. Antonie Equation was also used to predict the vapor pressures for other compounds [4, 5]. In this work, temperature of 310.9K (100F) was chosen for *T* in the predictions.

The total vapor pressure was calculated by summing up the partial pressure of each species in headspace vapor, p_i, calculated as described above. The headspace vapor speciation profile was then finalized by converting the mole fraction to weight fraction for each compound.

3 Results and Discussion

Isopentane accounts for about a third (29.3%) of headspace vapor mass. Ethanol is 9.3%, slightly less in the headspace than in the liquid fuel (10%). The other abundant species are alkanes with low molecular weights and high vapor pressures: n-butane, n-pentane, and 2-methylpentane. These five compounds account for almost 60% of the total headspace vapor. In profile OG661, total weight fraction of the five species is 10% more. This is mainly due to the relatively high isopentane content (37.3%) in OG661 (Figure 1). The details of OG691 are presented in Table 1.

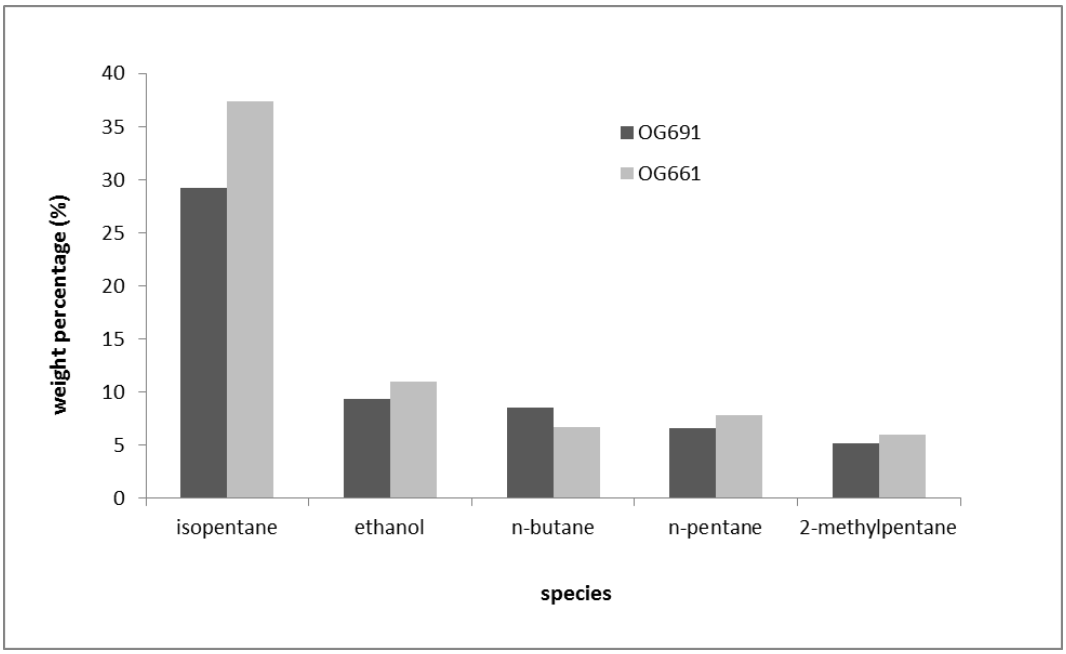

Figure 1. Comparison of major species in OG691 and OG661

The ROG/TOG ratio of Profile OG691 is 1.00. Assuming that the mass of FID-THC is based on the molecular weight of methane per carbon measured, the estimated TOG/THC fraction is 1.086. It can be used to converts THC emission mass to actual weight TOG.

Table 1. OG speciation profile for headspace vapor of E10 summer gasoline fuel

Species Name	*SAROAD*	*Weight Percentage (%)*
(2-methylpropyl)benzene	45235	0.001256
1,2,3,5-tetramethylbenzene	91104	0.001205
1,2,3-trimethylbenzene	45225	0.007058
1,2,4,5-tetramethylbenzene	91103	0.001039
1,2,4-trimethylbenzene	45208	0.039799
1,3,5-triethylbenzene	91117	0.000042
1,3,5-trimethylbenzene	45207	0.015565
1,4-diethylbenzene	45114	0.001988
1-butene	43213	0.127028
1-hexene	43245	0.731472
1-methyl-2-ethylbenzene	99915	0.010118
1-methyl-3-ethylbenzene	99912	0.036244
1-methyl-4-ethylbenzene	99914	0.015567
1-methyl-4-isopropylbenzene	91094	0.000298
1-methylnaphthalene	91124	0.000055
1-pentene	43224	0.640221
2,2,3,trimethylhexane	91059	0.000611
2,2,3-trimethylbutane	43160	0.026847
2,2,3-trimethylpentane	43296	0.020857
2,2,4-trimethylpentane	43276	1.543471
2,2,5-trimethylhexane	98033	0.122044
2,2-dimethylbutane	43291	1.922857
2,2-dimethylheptane	91056	0.016169
2,2-dimethylhexane	98138	0.010383
2,2-dimethylpropane	98130	0.059924
2,3,3-trimethyl-1-butene	91002	0.005915
2,3,3-trimethylpentane	43280	0.080524
2,3,4-trimethylpentane	43279	0.253597
2,3-dimethylbutane	98001	1.970534
2,3-dimethylhexane	98139	0.113851
2,4-dimethylhexane	43277	0.173207
2,4-dimethylpentane	43271	1.170439
2,5-dimethylhexane	43278	0.136359
2-methyl-1-butene	43225	0.015711
2-methyl-2-butene	43228	2.092053
2-methyl-2-pentene	98004	0.254863
2-methylheptane	98140	0.150428
2-methylhexane	43275	2.899476
2-methylnaphthalene	91123	0.000183
2-methyloctane	98146	0.022743
2-methylpentane	43229	5.172507
3,3-diethylpentane	91072	0.007697
3,3-dimethylhexane	98171	0.011552
3,4-dimethylhexane	98150	0.002496
3-ethylhexane	91039	0.062409
3-methyl-1-butene	43223	1.314331
3-methyl-3-ethylpentane	91036	0.010994
3-methyl-cis-2-pentene	98163	0.271372
3-methylheptane	43298	0.169998
3-methylhexane	43295	1.336755

3-methylpentane	43230	3.002839
4-methyl-cis-2-pentene	98170	0.039663
4-methylheptane	43297	0.074878
4-methyl-trans-2-pentene	43293	0.109574
Benzene	45201	0.549442
cis-1,2-dimethylcyclohexane	91055	0.022676
cis-1,3-dimethylcyclopentane	91018	0.296576
cis-2-butene	43217	0.662048
cis-2-hexene	98035	0.211970
cis-2-pentene	43227	0.801250
Cyclohexane	43248	0.350661
Cyclohexene	43273	0.028043
Cyclopentane	43242	4.024819
Cyclopentene	43292	0.321667
Ethanol	43302	9.317200
Ethylbenzene	45203	0.141423
ethylcyclohexane	43288	0.042815
ethylcyclopentane	98057	0.147169
Isobutene	43214	1.539439
Isobutylene	43215	0.079126
Isopentane	98132	29.247430
Isoprene	43243	0.026761
isopropylbenzene	98043	0.004279
isopropylcyclohexane	90120	0.001049
Isopropylcyclopentane	43178	0.003081
methylcyclohexane	43261	0.485884
methylcyclopentane	43262	2.287711
m-xylene	45205	0.267533
Naphthalene	98046	0.000597
n-butane	43212	8.563981
n-butylbenzene	91098	0.000715
n-decane	43238	0.002533
n-dodecane	43255	0.000075
n-heptane	43232	0.766864
n-hexane	43231	2.169322
n-nonane	43235	0.025848
n-octane	43233	0.082110
n-pentadecane	43260	0.000000
n-pentane	43220	6.570377
n-propyl alcohol	43303	0.030084
n-propylbenzene	45209	0.012262
n-tetradecane	43259	0.000002
n-tridecane	43258	0.000026
n-undecane	43241	0.000432
o-xylene	45204	0.125055
Propane	43204	0.167810
propylcyclopentane	90116	0.000376
p-xylene	45206	0.116709
t-butylbenzene	45215	0.002210
Toluene	45202	1.346700
trans-1,2-dimethylcyclopentane	91021	0.296607
trans-1,3-dimethylcyclopentane	91019	0.351190
trans-1,3-pentadiene	90100	0.015471

trans-2-butene	43216	0.582166
trans-2-octene	43263	0.003564
trans-2-pentene	43226	1.501344
trans-3-hexene	98136	0.126449
Total		*100.000000*

4 Estimated Impacts of the Profile Update on the Emission Inventory

The newly-developed profile OG691, will replace the current profile OG661 for the inventory categories associated with on-road gasoline vehicle resting loss, off-road equipment gasoline evaporative, and a variety of losses from petroleum marketing and petroleum storage for 2010 and later years as E10 fuel is in use. The related SCCs/EICs are summarized in Appendix.

The statewide annual average TOG emissions of gasoline vapor losses are 220.63 tons/day based on the 2009 Almanac projection for year 2010 [6]. Using the new profile OG691, the ROG will be 220.63 tons/day, which is 0.37% higher than the ROG estimated based on the current profile OG661; the emissions of benzene is increased by 53.16% (Table 2).

The ozone forming potential (OFP) is 2.34 gO3/gORG for OG691 calculated based on SAPRC07 mechanism; while it is 2.02 gO3/gORG for OG661.

Table 2. Changes on emissions of organic gas species for gasoline headspace vapor related categories (2010)

Statewide Annual Ave. Emissions		*Current OG661 (tons/day)*	*New OG691 (tons/day)*	*Change*	
				Emissions(tons/day)	*Percentage*
ROG		219.81	220.63	+0.82	+0.37%
Toxics	Benzene	0.79	1.21	+0.42	+53.16

5 Version Control

This section will be completed after management approval and after the CEIDARS FRACTION table and PMPROFILE table are updated. Version information from CEIDARS FRACTION table will be copied here.

References:

1. California Air Resources Board Main Speciation Profiles. In Jan 1, 2012 ed.; California Air Resources Board: 2012.
2. Allen, P.; Bradley, R.; Croes, B.; Luo, D.; Vincent, R.; Woodhouse, L. *Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline*; California Air Resources Board: November 18, 1999.

3. Harley, R. A.; Coulter-Burke, S. C.; Yeung, T. S., Relating Liquid Fuel and Headspace Vapor Composition for California Reformulated Gasoline Samples Containing Ethanol. *Environmental Science & Technology* **2000,** *34*, (19), 4088-4094.
4. Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P., *The Properties of Gases and Liquids*. Fifth ed.; McGraw-Hill, Inc.: 2001.
5. Reid, R. C.; Prausnitz, J. M.; Poling, B. E., *The Properties of Gases and Liquids*. McGraw-Hill, Inc.: 1987; p 741.
6. CEPAM. In California Air Resources Board: 2012.

Appendix

Table 1. SCCs/EICs associated with gasoline headspace vapor profile

7	40600144	85087211004055	86089111000041
207	40600147	85087211004153	86089211000041
307	40600151	85087211004155	86090111001153
11676	40600162	85087211004253	86090111001167
46466	40600163	85087211004255	86090111001169
46474	40600201	85087211004553	86090111001175
46482	40600226	85087211004555	86090111001185
46490	40600231	85087211004653	86090111001333
46516	40600232	85087211004655	86090111001345
46532	40600234	85087311003053	86090111001363
46540	40600236	85087311003055	86090111001375
46557	40600238	85087311003253	86090111002985
46581	40600239	85087311003255	86090111002995
46631	40600240	85087311003453	86090111004045
46730	40600241	85087311003455	86090111004065
47993	40600242	85087411000953	86090111004095
54213	40600301	85087411000955	86090111004103
54270	40600302	85087411001053	86090111004113
54312	40600303	85087411001055	86090111004125
82248	40600304	85087411001253	86090111005673
82792	40600305	85087411001255	86090111005685
82800	40600306	85087411001553	86090111005693
82818	40600307	85087411001555	86090111005705
82826	40600399	85087411001653	86090111005725
83121	40600401	85087411001655	86090111007605
83170	40600402	85087511002153	86090111007615
83485	40600403	85087511002155	86090111008105
83493	40600499	85087711005153	86090111008113
83501	40600601	85087711005155	86090111008345
83519	40600603	85087711005253	86090111008353
83527	40600707	85087711005255	86090111008365
83535	40729697	85087711005353	86090111008373
83543	31039016000000	85087711005355	86090111008385
84095	32032211200000	85087711005453	86090111009075
84111	32032411000000	86088311000021	86090111009543
84186	32039011000000	86088311000041	86090111009555
84202	32039211000000	86088411000041	86090111009835
84301	33032611100000	86088411009375	86090211001153
84327	33032611200000	86088511000021	86090211001167
84392	33032611300000	86088511000041	86090211001169
84418	33032811100000	86088611000021	86090211001175
84467	33032811200000	86088611000041	86090211001185
84483	33032811300000	86088611000145	86090211002985
84541	33036611000000	86088611000175	86090211002995
84566	33036811000000	86088611000205	86090211004045

84616	33037211000000	86088611000225	86090211004065
84632	33037411000000	86088611002855	86090211004095
84699	33037611000000	86088611002875	86090211004103
84715	33037811000000	86088611002905	86090211004113
86165	33038211000000	86088611002935	86090211004125
86181	33038211100000	86088611005503	86090211005673
86256	33038211200000	86088611005515	86090211005685
86272	33038211300000	86088611005535	86090211005693
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86728	33039011000000	86088611008855	86090211008113
86801	33039411000000	86088611008875	86090211008345
86827	33099511000000	86088611008895	86090211008353
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87080	71071011000000	86088711000021	86090211008385
87106	71071411000000	86088711000041	86090211009075
87171	71073811000000	86088711000655	86090211009543
87197	71074211000000	86088711000665	86090211009555
87254	72071011000000	86088711000675	86090211009835
87270	72071411000000	86088711000685	86090311001395
87346	72073811000000	86088711000835	86090311001405
87361	72074211000000	86088711000855	86090311004085
87460	72271011000000	86088711000875	86090311005745
87486	72271411000000	86088711000895	86090311005755
87551	72273811000000	86088711000915	86090411000385
87577	72274211000000	86088711001105	86090411000395
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40301182	77671011000000	86088711008595	86090611009755
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40301202	77673811000000	86088711009025	86090611009795
40400101	77674211000000	86088711009335	86099511000041
40400102	77771011000000	86088711009425	87089311000015
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40400117	84086411008013	86088911000705	87089311003915
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40400404	85087011006255	86088911004165	87089311008495
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40400406	85087011006555	86088911005655	87089311008665
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