California Environmental Protection Agency

Air Resources Board

Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline

Appendix A

Emissions

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A-1. Introduction

The photochemical modeling described in Appendix B requires emission inventories as input. We evaluated emission impacts for four fuel scenarios for calendar year 2003. The scenarios are:

- 2003 MTBE-based California Phase 2 Reformulated Gasoline (CaRFG).
- 2003 Ethanol-based fully complying fuel (with oxygen content of 2.0 wt%).
- 2003 Ethanol-based fully complying fuel (with oxygen content of 3.5 wt%).
- 2003 Non-oxygenated fully complying fuel.

In addition, we include emission data for 1997 MTBE-based CaRFG to serve as a link to observed air quality in the South Coast Air Basin (SoCAB).

We focused our analysis on emissions of the following air contaminants:

- Criteria pollutant precursors [carbon monoxide (CO), oxides of nitrogen (NO_X), and reactive organic gases (ROG)].
- Toxic air contaminants (acetaldehyde, benzene, 1,3-butadiene, and formaldehyde).
- Fuel oxygenates (ethanol and MTBE).
- Alkylates (C_6 to C_9 branched alkanes and cycloalkanes).
- Additional compounds of interest to OEHHA (*n*-hexane, isobutene, toluene, and xylene isomers).

In order to develop the emission estimates for 1997 and 2003, we developed organic gas emission profiles for each fuel and applied the profiles to all gasoline-related emission inventory categories (e.g., passenger cars, heavy-duty vehicles, fuel spillage, off-road mobile sources, etc.). The emission processes for which we developed profiles include:

- Liquid gasoline.
- Hot soak and running loss evaporative.
- Diurnal and resting loss evaporative.
- Start exhaust -- catalyst and non-catalyst.
- Stabilized exhaust -- catalyst and non-catalyst.

For 1997 MTBE-based CaRFG, we used organic gas emission profiles developed from ARB surveillance data and presented at a public workshop in September 1998 (ARB, 1998a). We used the results of a linear-programming refinery model study sponsored by the California Energy Commission (MathPro, 1998ab) to establish the liquid gasoline profiles. In general the MathPro (1998ab) study predicted significant removal of pentanes and an increased use of alkylates when MTBE is banned as a fuel oxygenate.

The liquid gasoline profiles were also applied to hot soak evaporative emissions for all the 2003 fuels as recommended from a peer review conducted by Professor Harley of the University of California

at Berkeley (see Attachment A1). Running loss evaporative emissions were also speciated using the liquid gasoline profiles. Professor Harley calculated headspace vapors for all the 2003 fuels from the liquid gasoline composition (see Attachment A1) and we applied these to diurnal and resting loss evaporative emissions for the MTBE-free scenarios.

The emission profiles for the exhaust categories were established by adjusting the profiles for the MTBE-based CaRFG adopted in September 1998 (ARB, 1998a). The exhaust adjustments maintain consistency with the fuel composition. The adjustments for isobutene, identified as a major byproduct of MTBE combustion in the University of California MTBE report (Koshland *et al.*, 1998), were based on analysis of results from the Auto/Oil Program (1991; 1995), the ATL (1995) study, and an ARB (1998b) study contrasting MTBE-based CaRFG with a non-complying ethanol-containing gasoline. In addition, we input the fuel properties into the ARB Predictive Model for exhaust emissions of benzene and 1,3-butadiene (ARB, 1995), and into newly created models for evaporative benzene emissions and exhaust emissions of acetaldehyde and formaldehyde that distinguish between MTBE and ethanol as the oxygenate (ARB, 1999b). These profiles went through several iterations and were peer reviewed by Professor Harley in June 1999 (see Attachment A1), and presented at public workshops on July 12 and October 4. What is presented here is substantially different from what was presented earlier, having been extensively revised after errors were found by the peer review of Professor Harley and during the public comment period.

In order to determine if the organic gas emission profiles are reasonable, we conducted a limited emission testing program at the ARB laboratory in El Monte. We tested three fuels:

- ARB commercial MTBE-based Phase 2 regular-grade gasoline.
- Tosco ethanol-blended regular-grade gasoline (with oxygen content of 2.05 wt%).
- Chevron non-oxygenated regular-grade gasoline.

We conducted full VOC speciation of the liquid gasoline, the headspace vapors, and exhaust tests of seven vehicles. The Tosco and Chevron gasolines are not representative of fuels expected to be sold in 2003, and we were not able to draw quantitative conclusions. In addition, most of the vehicles were aged, and several had unstable emission rates. With these limitations in mind, the test results are consistent, for several broad categories of organic gases, with the emission profiles prepared by ARB and by Professor Harley using limited data.

This appendix describes the organic gas emission profiles, the emission estimates, and the fuel and vehicle testing results.

A-2. Development of Organic Gas Emission Profiles

This section documents the organic gas speciation profiles used as inputs the photchemical modeling. We estimated profiles for gasoline blended with 2.0 wt% oxygen as ethanol, gasoline blended with 3.5 wt% oxygen as ethanol, and gasoline without any oxygen. There are profiles for compositions of the liquid fuels, evaporative emissions, and exhaust emissions.

A-2.1. MTBE-Based CaRFG Profiles

A series of motor vehicle related profiles were presented at a public workshop on September 10, 1998 (ARB, 1998a). The speciation profiles were all based on MTBE-based CaRFG, and included:

- Liquid gasoline.
- Headspace vapors.
- Start exhaust -- catalyst and non-catalyst.
- Stabilized exhaust -- catalyst and non-catalyst.

The liquid gasoline speciation is based on tests of MTBE-based CaRFG conducted by the ARB in 1996 and 1997 (ARB, 1998b). The headspace vapor speciation for the MTBE-based CARFG was the mathematically derived speciation using an equilibrium model (Kirchstetter and Harley, 1997). The exhaust speciation is based on 1996 surveillance vehicle tests (ARB, 1998b) using the methodology discussed by Allen (1997). Vehicles were randomly selected in the Southern California region for the surveillance tests, and were tested "as received".

A-2.2. Non-MTBE-Based CaRFG Profiles

A-2.2.1. Overview of Profile Development

For gasoline compositions, we created organic gas speciation profiles by adjusting the ARB composition profile for CaRFG blended with 11 vol% MTBE. The adjustments are based on comparisons of gasoline compositions among the model fuels predicted in a linear programming refinery modeling study conducted by MathPro (1998ab). However, the benzene content of the compositions has been held constant at the value in the ARB profile for MTBE-blended CaRFG.

For diurnal and resting loss evaporative emissions, the profiles for the ethanol-blended and non-oxygenated CaRFGs are the headspace vapor compositions predicted by Professor Harley for the corresponding gasoline compositions (see Attachement A3). For hot soak and running loss evaporative emissions, the profiles have been set equal to the corresponding gasoline compositions.

For exhaust emissions, we have created profiles by making certain adjustments to the corresponding ARB profiles for CaRFG blended with 11 vol% MTBE. Some of the adjustments to create profiles for ethanol-blended CaRFGs are based on comparisons between the emission compositions measured by ARB in its recent testing of an MTBE-blended CaRFG and a gasoline with 10 vol% ethanol (ARB, 1998b). Likewise, some of the adjustments to create exhaust profiles for the non-oxygenated gasoline are based on comparisons of emission compositions by the Auto/Oil Program (1991, 1995). Also, in part, the adjustments of all the exhaust profiles are based on comparisons among the model fuels predicted by MathPro.

The contents of the four toxic species in exhaust (acetaldehyde, benzene, 1,3-butadiene, and formaldehyde) for the ethanol-blended and non-oxygenated CaRFGs have been determined by adjustments to the corresponding profiles for MTBE-blended CaRFG. The adjustments are based on applying the ARB Predictive Model (including a draft new element that distinguishes between MTBE and ethanol in predicting aldehyde emissions) to the fuels predicted by MathPro.

It must be noted that, in the absence of extensive emission data taken with representative commercial fuels, the emission profiles for MTBE-free CaRFGs are uncertain. Therefore, differences in outputs from the photochemical model must be interpreted with caution. Small differences could easily be due to the uncertainties in the inputs.

The immediately following sections describe the derivations in more detail. Section A-2.2.6 gives explicit directions for adjusting the profiles for MTBE-blended CaRFG to produce the profiles for the other fuels.

A-2.2.2. Limited Utility of Empirical Data

The data from ARB (1998b) and the Auto/Oil Program (1991; 1995) studies were adequate only for determining the amount of isobutene to remove from the MTBE-based exhaust and for determining the amounts of ethanol that should be added to the exhaust emissions. Neither study was useful for dealing with other species that are important to reactivity. The non-MTBE test fuels in both studies were matched in chemical composition to the MTBE test fuels. Such matching is not realistic; if applied to current typical MTBE-blended CaRFG, it would create ethanol-blended gasolines that would violate the ARB Reid Vapor Pressure (RVP) limit and non-oxygenated gasolines that would be deficient in octane.

To maintain an adequate octane number in non-oxygenated gasolines, refiners will typically use much higher contents of alkylates than in today's MTBE-blended gasolines. According to the linear-programming results by MathPro (1998ab), branched alkanes will be more common in ethanol-blended CaRFGs, also. Adding ethanol at 3.5 wt% oxygen would essentially replace the octane. However, ethanol at 2.0 wt% oxygen would not provide sufficient octane, so additional octane-raising steps would be needed. These extra contents in the gasolines should be reflected in the emission streams.

Some exhaust and headspace data comparing commercially available CaRFGs have been taken recently in the ARB labs (see Section A-5). However, the seven vehicles used to test the fuels were generally not representative of the on-road fleet, and several showed large variability in NMOG emissions from test to test. Furthermore, the composition and RVP of the ethanol-blended CaRFG that was tested do not resemble the expected typical properties of ethanol-blended gasolines that will be in commercial production in 2003. Therefore, the recent empirical data have not been used in creating the profiles, but rather to provide a reality check on the relative increases and decreases in broad categories of compounds (see Section A-6).

A-2.2.3. Development of Gasoline Composition Profiles

Ethanol-Blended CaRFGs. Table 2.1 shows the available detail on the composition of the MTBE-blended and ethanol-blended CaRFGs predicted by MathPro (1998ab) for 2002. There are data for the entire fuels and for each fuel on the oxygenate-free basis. Note that MathPro modeled a single ethanol-blended gasoline with oxygen at 2.7 wt%.

Table 2.1. Compositions of CaRFGs Modeled by MathPro (vol%)

	MTBE-Blended[a]		EtOH-Blended[b]		
	actual	w/o MTBE	actual	w/o EtOH	No Oxygen[c]
***n*-Butane**	0.6	0.65	0.5	0.54	0.1
C_5 and C_6 alkanes	6.1	6.9	4.3	4.6	11.3
Alkylates (C_7 to C_9 branched alkanes)	14.4	16.3	28.4	30.1	32.5
Benzene	0.67	0.76	0.80	0.87	0.80
Total aromatics	24.0	27.1	20.0	21.7	20
Total olefins	4.3	4.9	2.9	3.1	5.0
Oxygenate	11.4	0.0	7.8	0.0	0
Other	39	43	35	38	30
Total	100.47	99.61	99.7	98.91	100
Oxgyen (wt%)	2.1	--	2.7	--	--

[a] **"Ref. 2002, 1, CARB" on page 3 of Exhibit 8, Refinery Modeling Task 3, PB300-98-013I.**

[b] **"BAS U, Alk-100, 1, CARB" on page 3 of Exhibit 8, Refinery Modeling Task 3, PB300-98-013I.**

[c] **"HRG30, 1, CARB" on page 3 of Exhibit 8, Refinery Modeling Task 3, PB300-98-013I.**

Note the contrasts between the MTBE- and ethanol-blended CaRFGs on the oxygenate-free basis. These changes include a significant removal of pentanes and an increased use of alkylates. The reduction of pentanes is expected for ethanol-blended CaRFG, regardless of the ethanol content, to meet the limit on RVP. The near doubling in alkylate content is reasonable for ethanol at 2.0 wt% oxygen because that amount of ethanol does not replace the octane provided by MTBE at 11 vol%. For ethanol at 3.5 wt% oxygen, the need for added alkylate is not clear. However, we have applied the above ratios to the 3.5 wt% oxygen gasoline, too. This may lead to an overestimation of the alkylate content (and an under-estimation of the average ozone-forming potential) of that fuel because the cost of alkylate will discourage refiners from using more than they need.

The MathPro (1998ab) predictions include a greater benzene content in the ethanol-blended CaRFG than in the MTBE-blended CaRFG. The benzene content of the fuel is an important parameter because benzene emissions are influential in the computation of overall toxic emissions and because the estimated evaporative benzene emissions are proportional to the benzene content of the fuel. However, this prediction for a single gasoline constituent is less certain than the predictions for entire classes of compounds. Also, proposed "Phase 3 CaRFG" regulatory changes (ARB, 1999a) would discourage such an increase in benzene. Therefore, we believe that it would not be appropriate to change the benzene content of the CaRFG according to the type or lack of oxygenate.

Accordingly, to create the composition profiles for both of the ethanol-blended CaRFGs, the ARB profile for MTBE-blended CaRFG has been adjusted by multiplying certain contents on the oxygenate-free basis as follows:

- C_4 alkanes by 0.54/0.65=0.83
- C_5 and C_6 alkanes by 4.6/6.9=0.67
- C_7-C_9 branched alkanes by 30.1/16.3=1.85
- Aromatic species (except benzene) by 21.7/27.1=0.80
- Olefinic species by 3.1/4.9=0.63

Ethanol has then been inserted into the profiles at 5.75 wt% (2.0 wt% oxygen) and at 10.1 wt% (3.5 wt% oxygen). In re-normalizing to sum to 100%, steps have been taken to preserve these ethanol contents and to preserve the benzene content at its value in the profile for MTBE-blended CaRFG.

Non-oxygenated CaRFG. Table 2.1 shows the available detail on the composition of the MTBE-blended and non-oxygenated CaRFGs predicted by MathPro (1998ab) for 2002. As with the ethanol blended gasoline, we see a near doubling of the alkylate content.

In conformity with the derivation just presented for the ethanol-blended CaRFGs, we have adjusted the ARB profile for MTBE-blended CaRFG by multiplying certain contents on the oxygenate-free basis as follows:

- C_5 and C_6 alkanes by 11.3/6.9=1.64
- C_7-C_9 branched alkanes by 32.5/16.3=1.99
- Aromatic species (except benzene) by 20.0/27.1=0.74

The MathPro (1998ab) analysis indicates that the butanes in the MTBE-blended gasoline would be replaced by butenes in the non-oxygenated gasoline. We doubt that this is realistic. Lacking reliable information on the butane content of non-oxygenated CaRFG, we have made no adjustment of butanes in the MTBE-blended gasoline compositions in creating the non-oxygenated gasoline composition.

The olefinic content was not adjusted. At re-normalization to sum to 100%, the benzene content was kept at its value in the MTBE-blended gasoline profile.

A-2.2.4. Development of Evaporative Emission Profiles

For diurnal and resting loss evaporative emissions, all the liquid gasoline profiles (MTBE-blended, both ethanol-blended, and non-oxygenated CaRFGs) were input to a headspace prediction model developed by Professor Harley (see Attachment A3). For hot soak and running loss evaporative emissions, the liquid gasoline profiles were used directly. Since the benzene contents of all the fuels have been maintained equal, the benzene contents of the hot soak and running loss emission profiles are identical, and the benzene contents of the diurnal and resting emission profiles are nearly constant.

A-2.2.5. Development of Exhaust Emission Profiles

For both the ethanol-blended and non-oxygenated CaRFGs, three separate sets of adjustments have been made to the exhaust profiles for MTBE-blended CaRFG: (1) reduction of MTBE and isobutene; (2) adjustment of the four toxic species (acetaldehyde, benzene, 1,3-butadiene, and formaldehyde); and (3) adjustments to reflect the differences among fuels that result from the derivations in Section A-2.2.3. Ethanol was added to the ethanol-blended CaRFG. Re-normalization to sum to

100% was carried out with preservation of the ethanol, toxic, and alkylate contents at the values determined by the adjustment procedures.

MTBE and Isobutene. Table 2.2 summarizes empirical data on the ratio of isobutene (a decomposition product of MTBE) in exhaust streams from MTBE-blended and MTBE-free gasolines. These numbers are fairly stable across studies, fuel type, and emission mode (starts versus stabilized exhaust). Therefore, we have used their mean, 0.53, to adjust the isobutene content in the ARB profiles for MTBE-blended CaRFG to yield the isobutene content in each exhaust profile for each non-MTBE CaRFG.

Table 2.2. Isobutene Ratios, Non-MTBE Gasoline to MTBE Gasoline

	ARB (1998b)	ATL (1995)	Auto/Oil (1991)	Auto/Oil (1995)
Starts (Bag 1 – Bag 2)				
EtOH-blended	**0.47**	**0.56**	**0.59**	
Non-oxygenated				**0.57**
Stabilized (Bag 2)				
EtOH-blended	**0.40**	**0.46**	**no data**	
Non-oxygenated				**0.68**

Toxic Emissions in Exhaust. The appropriate profile adjustments for benzene and 1,3-butadiene can be estimated with the ARB Predictive Model using as inputs the properties of the CaRFGs predicted by MathPro (1998ab) with benzene held constant. Using the MathPro (1998ab) MTBE-blended CaRFG as the baseline, one can predict the changes in the benzene/THC and 1,3-butadiene/THC ratios for ethanol-blended CaRFGs and non-oxygenated CaRFG. For the ethanol-blended gasoline, the 2.7 wt% oxygen in the predicted fuel has been replaced with 2.0 wt% and 3.5 wt% oxygen.

Since the ARB Predictive Model was developed mostly with data from MTBE-blended and non-oxygenated gasolines, it should not be used to predict aldehyde emissions for gasolines with ethanol. Therefore, we have re-regressed the Predictive Model database to construct new models for acetaldehyde and formaldehyde that distinguish between ethanol and MTBE as the source of oxygen. Applied to the MathPro fuels, these new models predict changes in acetaldehyde and formaldehyde for the ethanol-blended and non-oxygenated CaRFGs relative to the MTBE-blended CaRFG.

Table 2.3 and Table 2.4 show the results of these methods. [The columns headed by "Δ(xx/HC)" are the relative (%) changes of the profile contents for species xx.]

Table 2.3. Modeled Changes in Exhaust Benzene and 1, 3-Butadiene Fractions

(from ARB Predictive Model; FTP-composite predictions for Tech 4)

CaRFG[a]	DHC (%)	DBenz (%)	D(Benz/HC)[b] (%)	D1,3BD (%)	D(BD/HC)[b] (%)
EtOH, 2.0 wt% O_2	+0.9	-3.3	*-4*	-2.3	*-2*
EtOH, 3.5 wt% O_2	-1.1	-0.8	*0*	-2.3	*-1*
Non-oxygenate	+1.2	-11	*-12*	-0.8	*-2*

[a] **Fuel predicted by MathPro (1998ab); contrasted with MathPro's MTBE-blended CaRFG.**

[b] **Approximation: D(A/B)/(A/B) = DA/A - DB/B.**

Table 2.4. Modeled Changes in Aldehydes

(per oxygenate-specific models)

CaRFG[a]	DHC[b] (%)	DForm[c] (%)	D(Form/HC) (%)	DAcet[c] (%)	D(Acet/HC) (%)
EtOH, 2.0 wt% O_2	+0.9	-5	*-6*	+28	*+27*
EtOH, 3.5 wt% O_2	-1.1	-9	*-8*	+133	*+132*
Non-oxygenate	+1.2	-10	*-11*	-4	*-5*

[a] **Fuel predicted by MathPro (1998ab); contrasted with MathPro's MTBE-blended CaRFG.**

[b] **From the current Predictive Model.**

[c] **From draft oxygenate-specific models applied to the oxygen contents.**

The adjustments applied to both the ARB start and stabilized exhaust profiles for MTBE-blended CaRFG are shown in Table 2.5.

Table 2.5. Adjustments to TAC Fractions in Start and Stabilized Exhaust Profiles

CaRFG	Acetaldehyde	Benzene	1,3-Butadiene	Formaldehyde
EtOH, 2.0 wt% O_2	1.27	0.96	0.98	0.94
EtOH, 3.5 wt% O_2	2.32	1.0	0.99	0.92
Non-oxygenate	0.95	0.88	0.98	0.89

Branched Alkanes and Other Species. MathPro (1998ab) predicted a near doubling of the alkylate content in non-oxygenated CaRFG relative to MTBE-blended CaRFG. This information does not provide guidance on how much the amounts of alkylate species would increase in the exhaust streams, nor does it identify the specific species involved. However, a doubling of the C_7 to C_9 branched alkane contents should provide an upper bound on the effect in the exhaust. Accordingly,

each C_7 to C_9 branched alkane in the exhaust profiles for the MTBE-blended CaRFG has been doubled to represent exhaust for non-oxygenated CaRFG. (Recent testing by ARB of commercial fuels corroborates that exhaust contents of branched alkanes are proportional to the fuel contents as discussed in Section A-6).

Another issue is identifying the elements of the profiles that are to be displaced by the extra C_7 to C_9 branched alkanes. The adjustments just described for toxic species should not be allowed to be perturbed by additions to the alkanes. Also, since MathPro (1998ab) predicted higher C_5 and C_6 alkanes in the non-oxygenated CaRFG than in the MTBE-blended CaRFG, the added branched alkanes should not allowed to "dilute" them. Therefore, in adjusting the ARB exhaust profiles for MTBE-blended CaRFG, the added C_7 to C_9 branched alkanes have been allowed to displace olefinic contents (except 1,3-butadiene), aromatic contents (except benzene), alkanes other than C_5 and C_6, and aldehydes (except formaldehyde and acetaldehyde).

The above considerations apply also to the exhaust profiles for ethanol-blended CaRFG at 2.0 wt% oxygen. The ethanol-blended CaRFG modeled by MathPro (1998ab) has 1.85 times the alkylate content of the modeled MTBE-blended CaRFG. This factor has been applied to the C_7 to C_9 branched alkanes in the exhaust profiles for MTBE-blended CaRFG. However, the procedure for creating exhaust profiles for ethanol at 2.0 wt% oxygen differs somewhat from that for the non-oxygenated CaRFG, for two reasons:

- The C_5 and C_6 alkanes in MathPro's ethanol-blended gasoline are less than in the MTBE-blended gasoline.
- The presence of ethanol in a profile (versus no oxygenate content) will cause re-normalization to alter all contents differently than in the non-oxygenated case, except as specifically prevented for particular species.

Therefore, in the exhaust profiles for ethanol at 2.0 wt% oxygen, the added C_7 to C_9 branched alkanes have displaced olefinic contents (except 1,3-butadiene), aromatic contents (except benzene), all other alkanes, and aldehydes (except formaldehyde and acetaldehyde). Each C_7 to C_9 branched alkane has been fixed at 1.85 times its final value in the corresponding exhaust profile for MTBE-blended CaRFG.

No analogous changes have been made for the exhaust profiles for ethanol-blended CaRFG with 3.5 wt% oxygen. Recall that in creating the gasoline composition profile for the 3.5 wt% oxygen gasoline, extra branched alkanes have been added in the same amounts as added to the composition of the ethanol-blended CaRFG with 2.0 wt% oxygen. Since that step tends to cause an underestimation of the ozone-forming potential of the 3.5 wt% oxygen gasoline composition (see Section A-3), we think it would be inappropriate to further bias the modeling input set for the 3.5 wt% oxygen gasoline by adding low reactivity species to its exhaust profiles. While some such additions (or other changes) might occur for actual ethanol-blended CaRFGs with 3.5 wt% oxygen, there are no data to permit a quantification.

Ethanol. For the ethanol-blended CaRFGs, we estimated the appropriate amount of ethanol for the exhaust profiles from the ethanol contents measured in the ARB (1998b) emission comparison between MTBE-blended CaRFG and a splash-blended ethanol gasoline with 3.9 wt% oxygen. Figures 2.1 and 2.2 show emission profiles from that work. In Figure 2.1, the ethanol content of start exhaust is 6%. Under the assumption that the exhaust content is proportional to the fuel content, the estimated ethanol contents for CaRFGs with 2.0 wt% and 3.5 wt% oxygen are 3.0% and 5.3%, respectively.

These values have been inserted into the start exhaust profiles. Figure 2.2 shows analogous data for stabilized exhaust measurements. In this case, we have not directly used the measured ethanol content (0.5%) because both it and the MTBE content of the exhaust from the MTBE-blended gasoline (0.26%) appear unreasonably low compared to other data. Therefore, we have taken their ratio, 1.96, as the basis for adjustment factors to the ARB stabilized exhaust profile for MTBE-blended CaRFG. Under the assumption of linearity with oxygen content, the adjustment factors for CaRFGs with 2.0 wt% and 3.5 wt% oxygen are 1.00 and 1.75, respectively.

A-2.2.6. Specifications for Creating Profiles

There is a different set of profiles for catalyst and non-catalyst exhaust emission. The following procedures for exhaust speciation apply to both categories.

A-2.2.6.1. Ethanol-Blended CaRFGs

A-2.2.6.1.1. Gasoline Composition

Remove MTBE from the ARB profile for MTBE-blended CaRFG. Multiply the following species by the indicated factors:

- *n*-butane -- 0.83
- Olefinic species -- 0.63
- C_7-C_9 branched alkanes -- 1.85
- C_5 and C_6 alkanes -- 0.67
- Aromatic species (except benzene) -- 0.80

For ethanol-blended CaRFG with 2.0 wt% oxygen, adjust all species in proportion so that their sum is [94.25% - benzene content] and insert 5.75 wt% ethanol plus the final benzene content. For ethanol-blended CaRFG with 3.5 wt% oxygen, adjust all species in proportion so that their sum is [89.1% - benzene content] and insert 10.1 wt% ethanol plus the final benzene content. In both cases, "final benzene content" is the fraction of benzene in the ARB profile for MTBE-blended CaRFG.

A-2.2.6.1.2. Hot Soak and Running Loss Evaporative Emissions

Use the gasoline compositions in Section A-2.2.6.1.1.

A-2.2.6.1.3. Diurnal and Resting Loss Evaporative Emissions

Use the headspace compositions for the two gasoline compositions in Section A-2.2.6.1.1 calculated by Professor Harley.

A-2.2.6.1.4. Starting Exhaust Emissions

For oxygen at 2.0 wt%, remove MTBE, methanol, and ethanol from the starting exhaust profile for MTBE-blended CaRFG. Multiply isobutene by 0.53. Adjust all species in proportion to sum to [100% minus the sum of final toxic species contents minus the total final C_7- C_9 branched alkane content and minus 3.0% ethanol]. The final toxic species contents are the contents in the starting exhaust profile for MTBE-blended CaRFG times the following factors:

- Acetaldehyde -- 1.27
- Benzene -- 0.96
- 1,3-Butadiene -- 0.98
- Formaldehyde -- 0.94

For each C_7 to C_9 branched alkane, the final content is the value in the starting exhaust profile for MTBE-blended CaRFG times 1.85. Insert the final toxic species contents, the final branched alkane contents, and 3.0% ethanol.

For oxygen at 3.5 wt%, remove MTBE and methanol from the starting exhaust profile for MTBE-blended CaRFG . Multiply isobutene by 0.53. Adjust all species in proportion to sum to [100% minus the sum of final toxic species contents and minus 5.3% ethanol]. The final toxic species contents are the contents in the starting exhaust profile for MTBE-blended CaRFG times the following factors:

- Acetaldehyde -- 2.32
- Benzene -- 1.00
- 1,3-Butadiene -- 0.99
- Formaldehyde -- 0.92

Insert the final toxic species contents and 5.3 wt% ethanol.

A-2.2.6.1.5. Stabilized Exhaust Emissions

For oxygen at 2.0 wt%, remove MTBE and methanol from the stabilized exhaust profile for MTBE-blended CaRFG . Multiply isobutene by 0.53. Adjust all species in proportion to sum to [100% minus the sum of final toxic species contents minus the total final C_7 to C_9 branched alkane content and minus the final ethanol content]. The final toxic species contents are the contents in the starting exhaust profile for MTBE-blended CaRFG times the following factors:

- Acetaldehyde -- 1.27
- Benzene -- 0.96
- 1,3-Butadiene -- 0.98
- Formaldehyde -- 0.94

For each C_7 to C_9 branched alkane, the final content is the value in the stabilized exhaust profile for MTBE-blended CaRFG times 1.85. The final ethanol content is 1.00 times the MTBE content of the stabilized exhaust profile for MTBE-blended CaRFG.

Insert the final toxic species contents, the final branched alkane contents, and the final ethanol content.

For oxygen at 3.5 wt%, remove MTBE and methanol from the stabilized exhaust profile for MTBE-blended CaRFG . Multiply isobutene by 0.53. Adjust all species in proportion to sum to [100% minus the sum of final toxic species contents and minus the final ethanol content]. The final toxic species contents are the contents in the stabilized exhaust profile for MTBE-blended CaRFG times the following factors:

- Acetaldehyde -- 2.32
- Benzene -- 1.00
- 1,3-Butadiene -- 0.99
- Formaldehyde -- 0.92

The final ethanol content is 1.75 times the MTBE content of the stabilized exhaust profile for MTBE-blended CaRFG.

Insert the final toxic species contents and the final ethanol content.

A-2.2.6.2. Non-Oxygenated CaRFG

A-2.2.6.2.1. Gasoline Composition

Remove MTBE from the ARB profile for MTBE-blended CaRFG. Multiply the following species by the indicated factors:

- C_5 and C_6 alkanes -- 1.64
- C_7-C_9 branched alkanes -- 1.99
- Aromatic species (except benzene) -- 0.74

Adjust all species in proportion so that their sum is [100% - benzene content]. Insert the benzene content equal to the benzene fraction of the MTBE-blended CaRFG

A-2.2.6.2.2. Extended Diurnal and Resting Loss Evaporative Emissions

Use the headspace compositions for the gasoline composition in Section A-2.2.6.2.1 calculated by Professor Harley.

A-2.2.6.2.3. Hot Soak and Running Loss Evaporative Emissions

Use the gasoline compositions in Section A-2.2.6.2.1.

A-2.2.6.2.4. Starting Exhaust and Stabilized Exhaust Emissions

Remove MTBE, methanol, and C_5 and C_6 alkanes from the starting exhaust or stabilized exhaust profile for MTBE-blended CaRFG. Multiply isobutene by 0.53. Adjust all species in proportion to sum to [100% minus the extracted C_5 and C_6 alkanes minus the sum of final toxic species contents minus the total C_7 - C_9 branched alkane content]. The final toxic species contents are the contents in the starting exhaust profile for MTBE-blended CaRFG times the following factors:

- Acetaldehyde -- 0.95
- Benzene -- 0.88
- 1,3-Butadiene -- 0.98
- Formaldehyde -- 0.89

For each C_7 - C_9 branched alkane, the final content is the value in the stabilized exhaust profile for MTBE-blended CaRFG times 2.0.

Insert the extracted C_5 and C_6 alkane contents, the final toxic species contents, and the final branched alkane contents.

A-2.3. CO Emissions

CO emissions are modeled as decreasing by 7.5% when oxygen is raised from 2.0 wt% (in the MTBE-blended CaRFG) to 3.5 wt% and as increasing by 5% when the oxygen is eliminated. It was left unchanged for ethanol-blended CaRFG with 2.0% oxygen.

The 7.5% increase for the higher oxygen content has been derived from data taken by ARB under the REPO5 test cycle (ARB, 1998b). According to FTP testing, the decrease in the CO inventory would be about 2.5% if oxygen were increased from 2.0 to 3.5 wt% of gasoline. However, the REPO5 data indicate that under "off-cycle" (non-FTP) operation, CO emissions are reduced much more. The staff has estimated the actual CO inventory reduction as 2.8 times the value calculated from FTP data. In contrast, available data do not show a difference between FTP and off-cycle testing in the effect of eliminating oxygen from gasoline. Therefore, the increase in the CO inventory estimated from FTP data, 5%, has been applied for the oxygen-free fuel.

Figure 2.1 "Starts" Comparison-ARB "MTBE-EtOH" Data

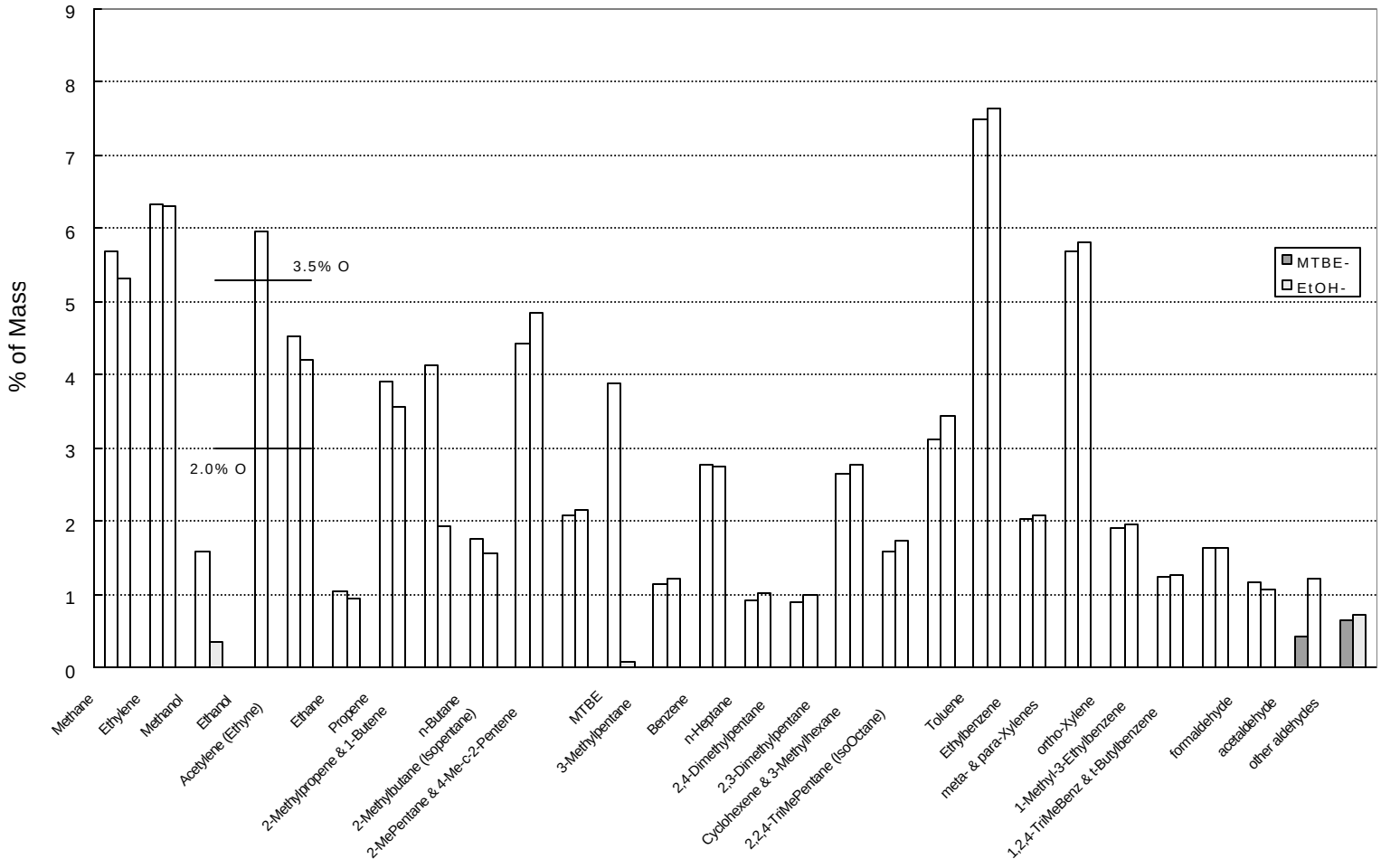
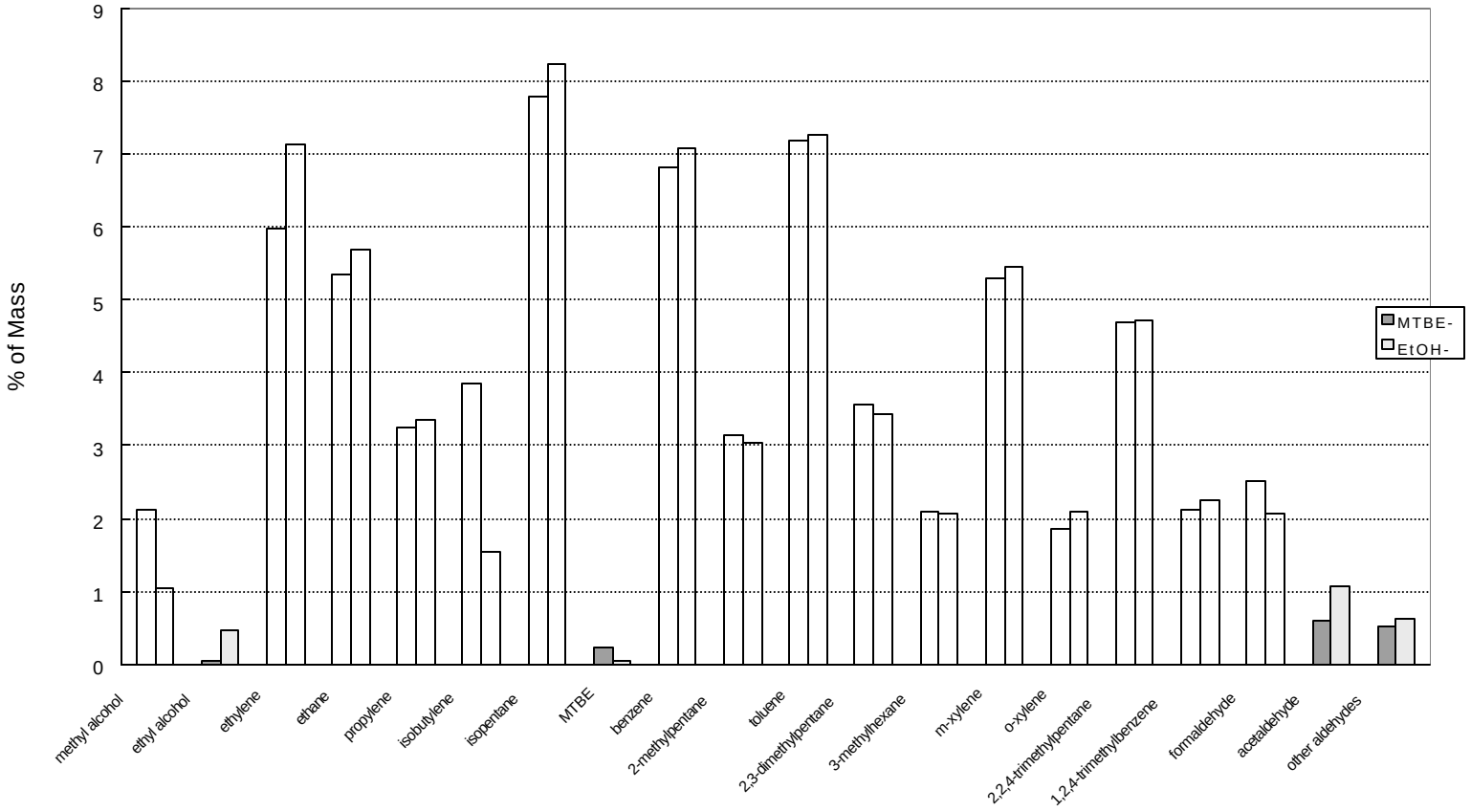


Figure 2.2. Bag 2 Comparison-ARB "MTBE-EtOH" Data (no methane)



A-3. Organic Gas Emission Profiles

Summaries of several important characteristics of the organic gas emission profiles derived in the preceding section are shown in Table 3.1 through Table 3.7. Table 3.1 through Table 3.6 compare the weight percent of six selected organic gas species (ethanol, benzene, formaldehyde, acetaldehyde, 1,3-butadiene, and methane) for all categories and gasolines used in the photochemical modeling.

Table 3.1 shows the weight percent of ethanol in the motor vehicle emission categories. Ethanol is not present in any of the non-oxygenated gasoline emission categories. A very small amount of ethanol is in the MTBE gasoline exhaust emissions as measured in ARB surveillance testing. Table 3.2 shows the estimated benzene weight percent for the emission categories. Since there is no difference expected in the benzene content in any of the gasolines, there is not much difference in the expected benzene in any of the MTBE-free categories.

Table 3.3 through Table 3.6 show acetaldehyde, formaldehyde, 1,3-butadiene, and methane. These compounds are not found in the gasoline nor in the evaporative emissions, so only the exhaust comparisons are shown. Since acetaldehyde is a product of ethanol combustion, it is expected to be higher as the ethanol content of gasoline increases. As seen in Table 3.3, acetaldehyde emissions are expected to be highest for the ethanol blends. Formaldehyde emissions are highest for the MTBE-blended gasoline as shown in Table 3.4. In Table 3.5, exhaust emissions of 1,3-butadiene are similar for all four gasolines.

Organic gas emission inventories include methane, which has a very low reactivity. Therefore, the methane fraction is very important in determining overall reactivity of the TOG emissions. Methane fractions are expected to decrease for the catalyst stabilized emission category as the vehicle fleet becomes cleaner over time. ARB studies have estimated that the average fleet methane fraction for 2003 will be approximately 18.7%. Photochemical simulations for 2003 were based on this methane estimate for catalyst stabilized exhaust. All other compounds were adjusted slightly by an equal percentage to yield a species profile totaling to 100%. All comparisons of profiles in this document are based on 1996 emission profiles (Allen, 1997). These profiles are the best organic gas speciation profiles to represent fleet emissions, since the 1996 surveillance data is used as the basis of the exhaust TOG emission speciation.

Table 3.7 shows the specific reactivity for all emission categories. The maximum incremental reactivity (Carter, 1994) values used to calculate the specific reactivity for each category are the same as those adopted for use in the ARB Low Emission Vehicle program and developed using the SAPRC90 chemical mechanism. Table 3.8 shows the ARB organic gas profile assignments for each emission category.

Figure 3.1 through Table 3.6 show a more complete comparison of the species profiles for each emission category. There are about 180 organic species identified in motor vehicle emissions. These figures contain seven categories of "lumped" species (butanes, pentanes, C_6+ alkanes, etc.) and eleven explicit species. Figure 3.1 and Figure 3.2 show the profiles for the liquid gasoline and headspace vapors. The non-noxygenated gasoline has the highest alkane and lowest aromatic content. The remaining figures are for catalyst and non-catalyst vehicle exhaust emissions. The largest difference in exhaust gas composition is due to the increased alkanes in the ethanol-blended gasoline with 2.0 wt%

oxygen and the non-oxygenated gasolines. The replacement of MTBE with ethanol leads to higher ethanol and acetaldehyde emissions.

Attachment A1 displays the complete speciation profiles for all categories of gasoline organic gas emissions used in the photochemical modeling.

Table 3.1. Ethanol Emissions (wt%)

Ethanol	Liquid	Hot Soak	Headspace	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	**0.00**	**0.00**	**0.00**	**0.09**	**0.07**	**0.06**	**0.01**
Non-Oxygenate	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
EtOH 2.0%	**5.75**	**5.75**	**9.35**	**3.00**	**2.01**	**3.00**	**1.86**
EtOH 3.5%	**10.10**	**10.10**	**9.56**	**5.28**	**3.58**	**5.28**	**3.24**

Table 3.2. Benzene Emissions (wt%)

Benzene	Liquid	Hot Soak	Headspace	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	**1.00**	**1.00**	**0.36**	**2.47**	**2.73**	**2.75**	**3.44**
Non-oxygenate	**1.00**	**1.00**	**0.69**	**2.17**	**2.40**	**2.42**	**3.03**
EtOH 2.0%	**1.00**	**1.00**	**0.80**	**2.37**	**2.62**	**2.64**	**3.30**
EtOH 3.5%	**1.00**	**1.00**	**0.80**	**2.43**	**2.73**	**2.74**	**3.45**

Table 3.3. Acetaldehyde Emission (wt%)

Acetaldehyde	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	**0.40**	**0.25**	**0.35**	**0.75**
Non-oxygenate	**0.38**	**0.24**	**0.33**	**0.71**
EtOH 2.0%	**0.51**	**0.32**	**0.44**	**0.95**
EtOH 3.5%	**0.91**	**0.58**	**0.81**	**1.74**

Table 3.4. Formaldehyde Emission (wt%)

Formaldehyde	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	**1.31**	**1.76**	**1.46**	**3.12**
Non-oxygenate	**1.17**	**1.57**	**1.30**	**2.78**
EtOH 2.0%	**1.23**	**1.65**	**1.37**	**2.93**
EtOH 3.5%	**1.19**	**1.62**	**1.34**	**2.88**

Table 3.5. 1,3-Butadiene Emissions (wt%)

1,3-Butadiene	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	0.70	0.57	0.78	0.83
Non-oxygenate	0.69	0.56	0.76	0.81
EtOH 2.0%	0.69	0.56	0.76	0.81
EtOH 3.5%	0.68	0.56	0.77	0.82

Table 3.6. Methane Emissions (wt%)

Methane	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	5.28	15.82	6.53	5.58
Non-oxygenate	4.79	14.57	5.95	5.16
EtOH 2.0%	4.82	14.75	5.96	5.19
EtOH 3.5%	5.20	15.85	6.52	5.59

Table 3.7. Specific Reactivity

Specific Reactivity	Liquid	Hot Soak	Headspace	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	2.54	2.54	1.58	3.61	3.53	3.50	3.97
Non-oxygenate	2.16	2.16	1.66	3.39	3.30	3.32	3.72
EtOH 2%	2.30	2.30	1.66	3.41	3.33	3.33	3.75
EtOH 3.5%	2.25	2.25	1.64	3.60	3.48	3.50	3.94

Table 3.8. Organic Gas Profile Assignment

Specific Reactivity	Liquid	Hot Soak	Headspace	Catalyst Start Exhaust	Catalyst Hot Exhaust	Non-cat Start Exhaust	Non-cat Hot Exhaust
MTBE	419	419	906	877	876(441)	402	401
Non-oxygenate	650	650	449	643	642(636)	641	640
EtOH 2%	660	660	450	649	648(637)	647	646
EtOH 3.5%	670	670	451	674	673(677)	676	675

Figure 3.1. Liquid Gasoline

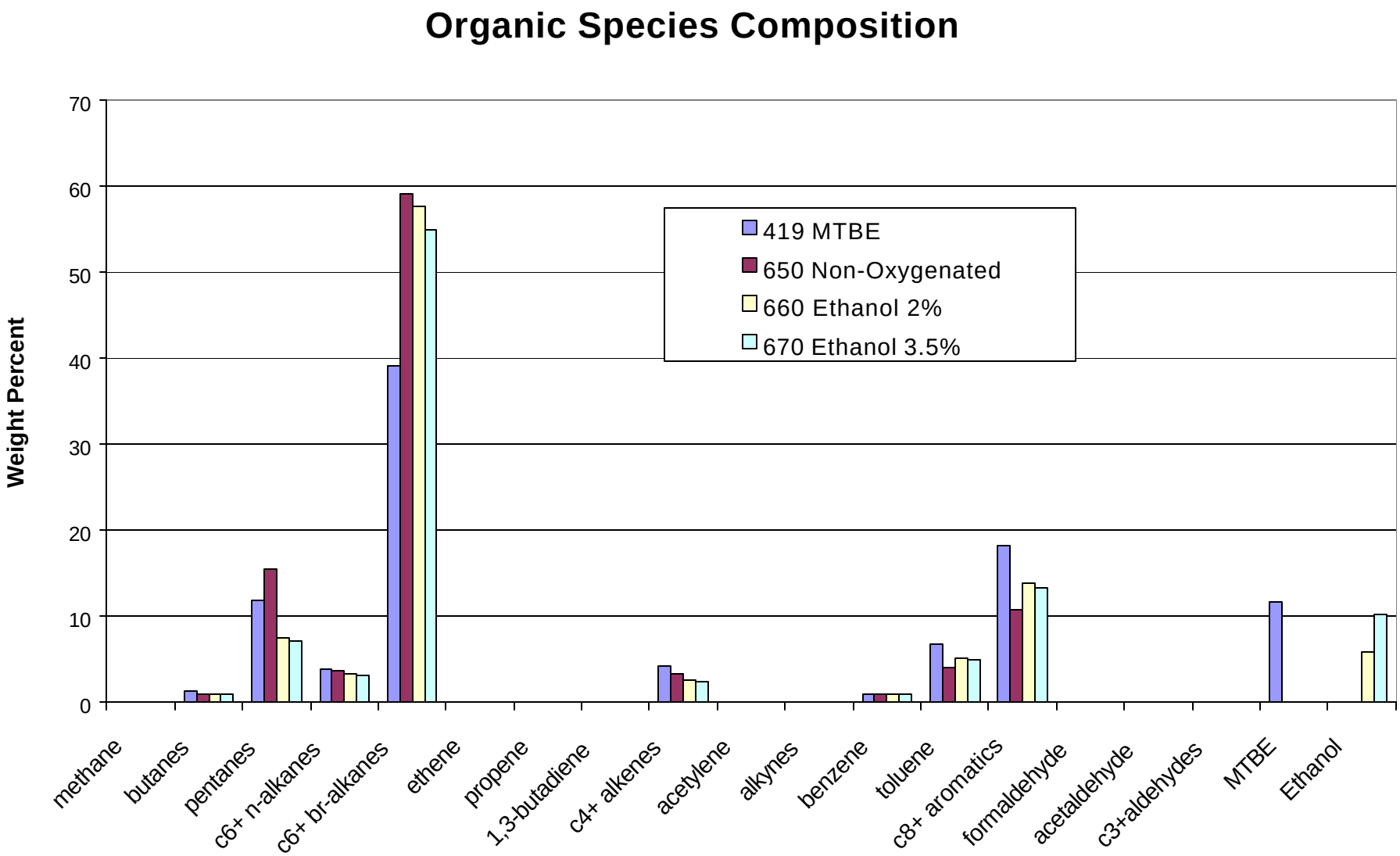


Figure 3.2. Headspace Vapors

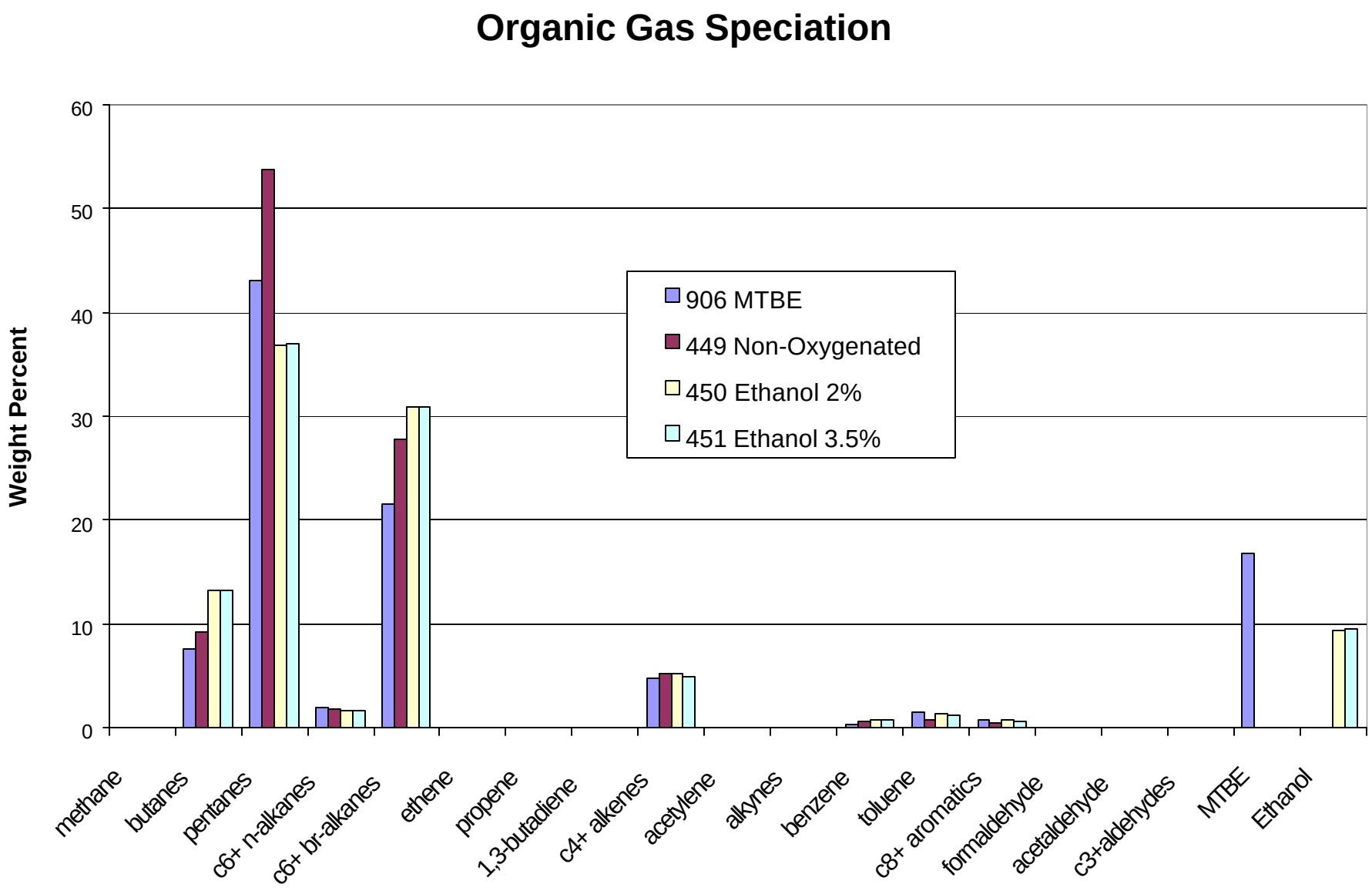


Figure 3.3. Catalyst Stabilized Exhaust

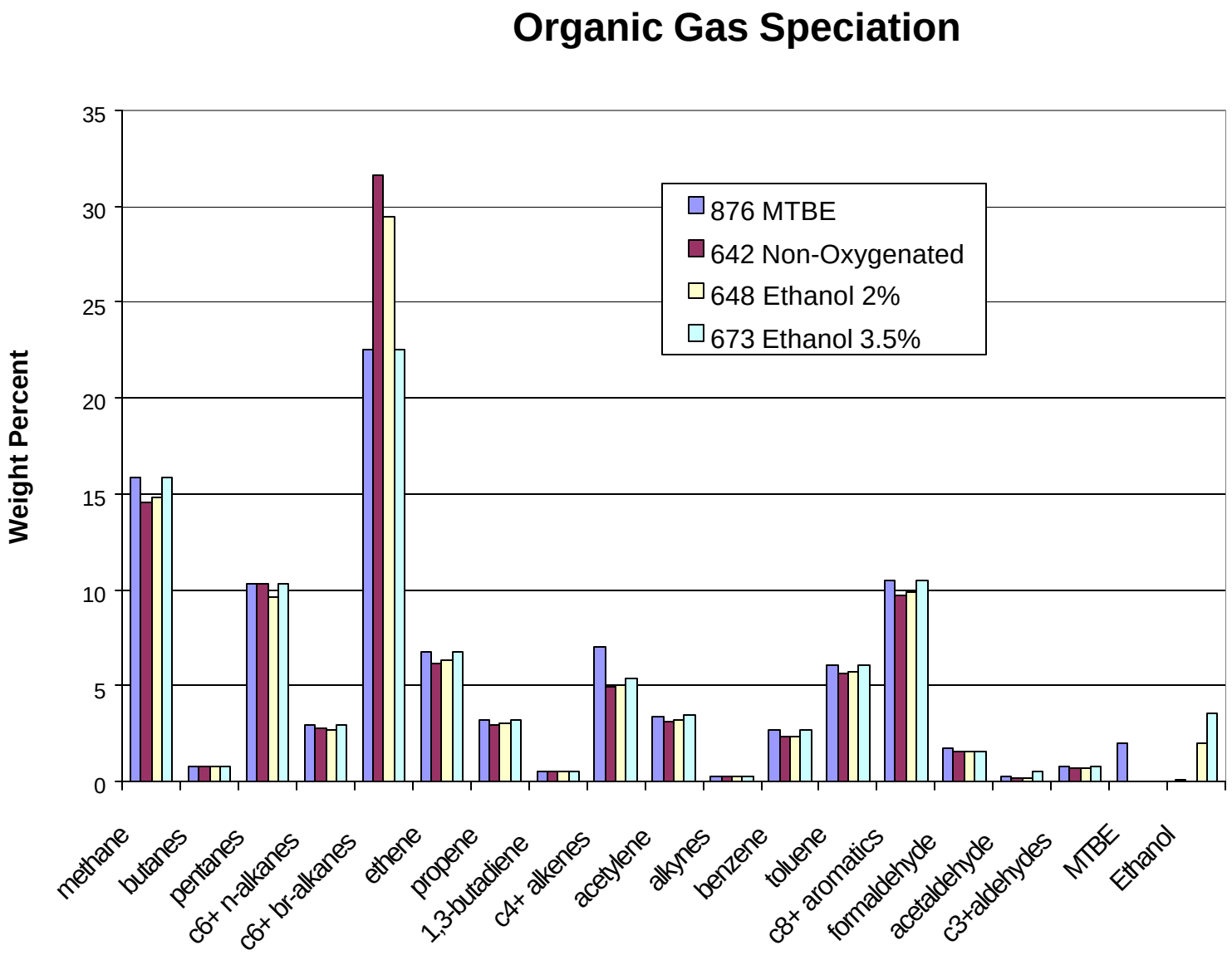


Figure 3.4. Catalyst Start Exhaust

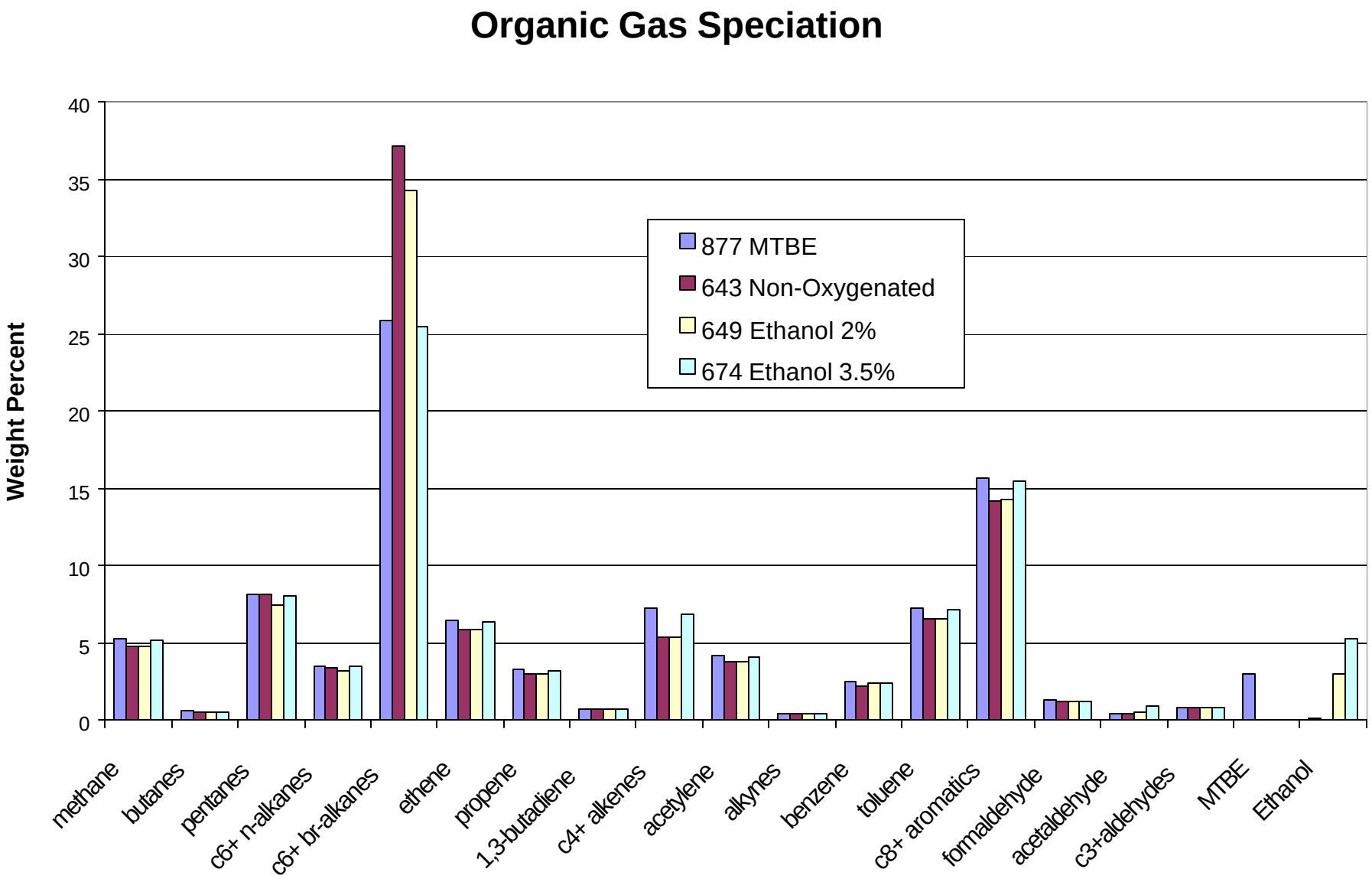


Figure 3.5. Non-Catalyst Stabilized Exhaust

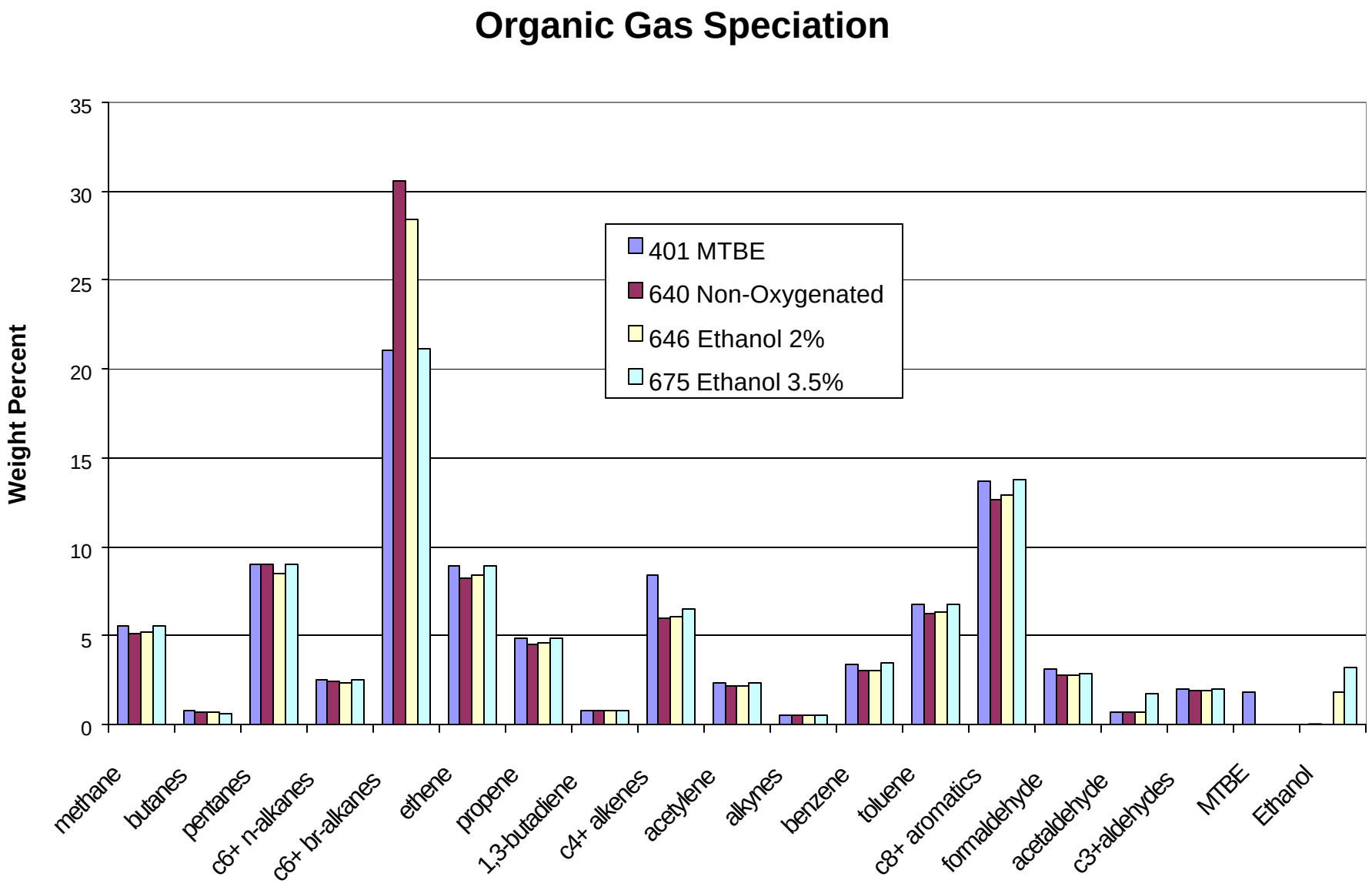
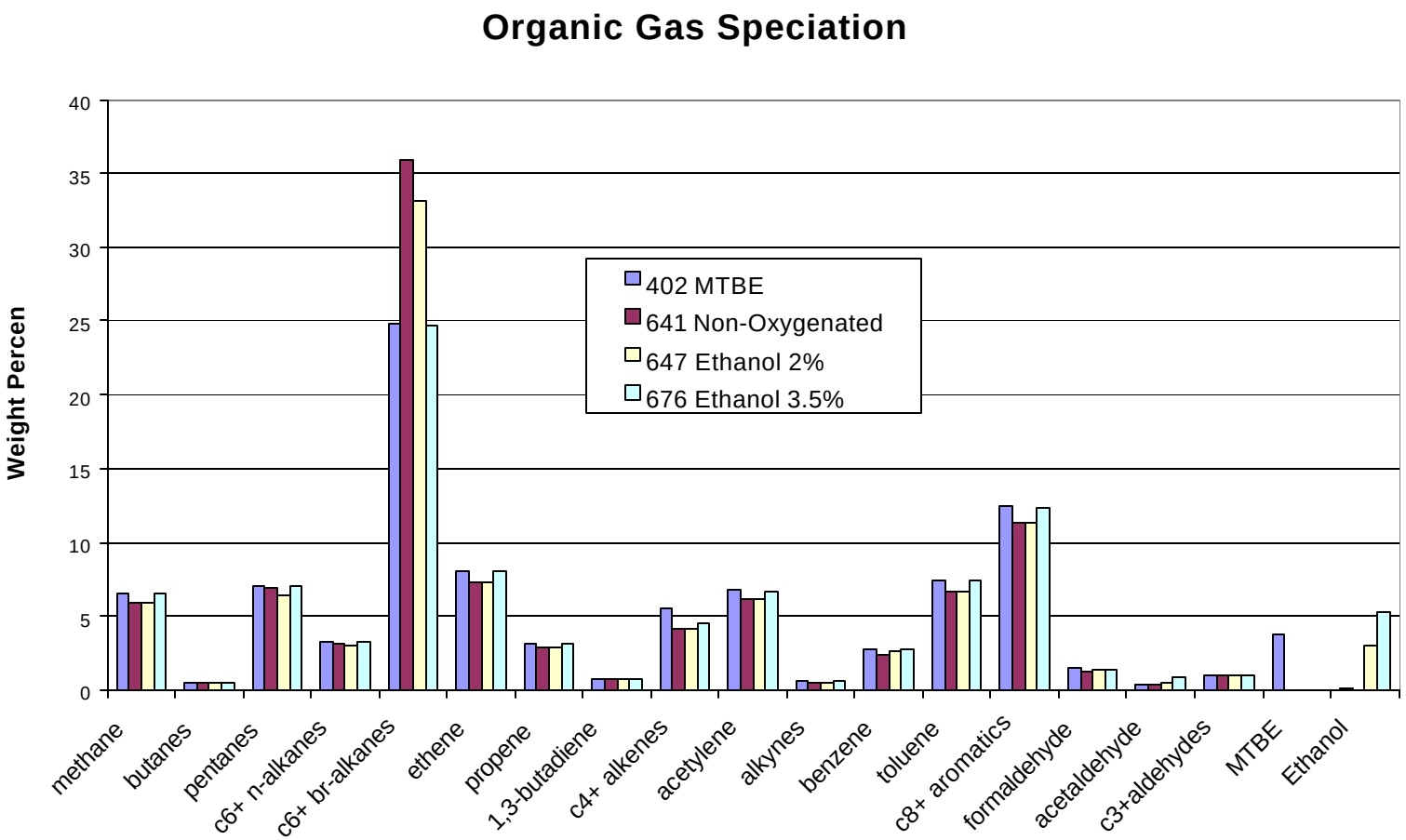


Figure 3.6. Non-Catalyst Start Exhaust



A-4. Emission Inventories

The development of emission estimates for each of the fuel scenarios involved a number of steps. This section briefly outlines the procedures used and presents detailed emission inventories for all the scenarios.

A-4.1. County-Level Emission Inventories

The inventories for the 1997 and 2003 baseline fuels (MTBE blends) were obtained from the ARB emission inventory database -- California Emissions Forecasting System (CEFS). These inventories are available at the county level. The inventories are the ozone planning inventories which reflect emissions on a summer day with high ozone. Since the official ARB inventory is updated regularly as better information becomes available, it is important to document the date of data retrieval. Area sources, including on-road and other mobile sources, were produced on May 26, 1999. Point sources were produced on June 10, 1999.

The on-road motor vehicle portion of the inventory was based on the Motor Vehicle Emission Inventory model MVEI7G (version 1.0c) because EMFAC2000 (ARB, 1999c) was not available. The off-road mobile source emissions were prepared with methodologies used previous to the development of the new ARB off-road emissions model.

These inventories represent mass emissions of principal criteria pollutants in units of tons per day. The pollutants include total organic gases, oxides of nitrogen, oxides of sulfur, carbon monoxide, and particulate matter. Estimates of emissions of individual organic gas constituents such as benzene were developed by combining the organic gas mass emissions from the inventory with the speciation profiles described earlier.

Table 4.1 through Table 4.5 present the summer ozone planning inventories for the South Coast Air Basin for each of the fuel scenarios. The pollutants of major interest include carbon monoxide (CO), nitrogen oxides (NO_X), reactive organic gases (ROG), benzene, 1,3-butadiene, acetaldehyde, formaldehyde, ethanol, and methyl *tertiary*-butyl ether (MTBE). In addition, emission inventory data for total alkylates and five additional VOCs (list) are presented in Table 4.6. The compounds in Table 4.6 were judged to be of minimal concern as discussed in Appendix C and were not modeled separately.

Table 4.1. 1997 MTBE-Based California Phase 2 Reformulated Gasoline (CaRFG)

South Coast Air Basin Emissions Tons/Day 27-Oct-99

Scenario: MTBE Summer 1997	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
STATIONARY SOURCES									
FUEL COMBUSTION									
ELECTRIC UTILITIES	3.87	16.58	.88	.061	.	.011	.146	.	
COGENERATION	2.79	6.89	.61	.007	.	.002	.053	.	
OIL AND GAS PRODUCTION (COMBUSTION)	1.57	10.66	.81	.031	.	.002	.095	.	
PETROLEUM REFINING (COMBUSTION)	8.56	17.72	1.4	.02	.002	.002	.139	.	.004
MANUFACTURING AND INDUSTRIAL	16.78	43.99	4.94	.211	.004	.071	.625	.	.002
FOOD AND AGRICULTURAL PROCESSING	.46	1.21	.2	.016	.	.	.033	.	.
SERVICE AND COMMERCIAL	12.78	26.27	3.48	.103	.002	.044	.394	.	.002
OTHER (FUEL COMBUSTION)	4.14	2.89	.6	.016	.004	.003	.032	.	.007
FUEL COMBUSTION - Subtotal	50.95	126.21	12.92	.466	.011	.136	1.518	.	.014
WASTE DISPOSAL									
SEWAGE TREATMENT	.03	.	.09				.014		
LANDFILLS	.55	.54	1.32				.044		
INCINERATORS	.12	.34	.01	.006			.		
OTHER (WASTE DISPOSAL)	.	.01	.79	.					
WASTE DISPOSAL - Subtotal	.7	.89	2.21	.006			.058		
CLEANING AND SURFACE COATINGS									
LAUNDERING	.	.	.64						
DEGREASING	.	.	85.53						
COATINGS AND RELATED PROCESS SOLVENTS	.22	.36	92.98	.069				1.965	.001
PRINTING	.02	.07	5.05					.53	
OTHER (CLEANING AND SURFACE COATINGS)	.	.	13.38	.003			.	.003	
CLEANING AND SURFACE COATINGS - Subtotal	.24	.43	197.56	.071			.	2.498	.001
PETROLEUM PRODUCTION AND MARKETING									
OIL AND GAS PRODUCTION	.02	.06	12.4	.187			.		.001
PETROLEUM REFINING	6.28	10.93	8.99	.13			.014		.134
PETROLEUM MARKETING	.08	.	23.57	.145					3.197
OTHER (PETROLEUM PRODUCTION AND MARKETING)	.05	.01	.2	.004					.001
PETROLEUM PRODUCTION AND MARKETING - Subtotal	6.43	11.01	45.16	.466			.014		3.334
INDUSTRIAL PROCESSES									
CHEMICAL	.04	.57	13.75	.001			.	.001	
FOOD AND AGRICULTURE	.21	.12	3.19					1.04	
MINERAL PROCESSES	2.67	9.93	.58						
METAL PROCESSES	1.74	.69	.65						
WOOD AND PAPER	.	.	.04						
GLASS AND RELATED PRODUCTS	.	1.48	.03						
OTHER (INDUSTRIAL PROCESSES)	1.4	1.15	2.61	.			.335		.
INDUSTRIAL PROCESSES - Subtotal	6.06	13.94	20.84	.001			.336	1.041	.

Table 4.1. 1997 MTBE-Based California Phase 2 Reformulated Gasoline (CaRFG) (continued)

	South Coast Air Basin Emissions Tons/Day								27-Oct-99
Scenario: MTBE Summer 1997	CO	NO_X	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
STATIONARY SOURCES - Subtotal	64.38	152.49	278.71	1.011	.011	.136	1.926	3.539	3.349
AREA-WIDE SOURCES									
SOLVENT EVAPORATION									
CONSUMER PRODUCTS	.	.	87.13				.029	25.241	
ARCHITECTURAL COATINGS AND RELATED PROCESS SOLVENTS	.	.	68.02	.067				.252	
PESTICIDES/FERTILIZERS	.	.	13.81	.596			.002	1.557	
ASPHALT PAVING	.	.	.48						
OTHER (SOLVENT EVAPORATION)	.	.	.17	.002					
SOLVENT EVAPORATION - Subtotal	.	.	169.61	.665			.031	27.05	
MISCELLANEOUS PROCESSES									
RESIDENTIAL FUEL COMBUSTION	40.78	22.65	2.75	.068		.173	.322		
FARMING OPERATIONS	.	.	10.92					2.731	
FIRES	7.54	.18	.53						
WASTE BURNING AND DISPOSAL	17.7	.74	1.39		.021				
UTILITY EQUIPMENT	229.58	.3	14.74	.55	.133	.12	.499	.002	.297
OTHER (MISCELLANEOUS PROCESSES)	.04	.24	1.7						
MISCELLANEOUS PROCESSES - Subtotal	295.65	24.11	32.03	.618	.153	.293	.821	2.732	.297
AREA-WIDE SOURCES - Subtotal	295.65	24.11	201.64	1.283	.153	.293	.852	29.782	.297
MOBILE SOURCES									
ON-ROAD MOTOR VEHICLES									
CATALYST COLD EXHAUST	1150.4	90.72	117.17	3.091	.876	.501	1.639	.113	3.779
CATALYST HOT EXHAUST	1832.7	327.43	107.86	3.55	.742	.326	2.289	.092	2.615
NON-CATALYST COLD EXHAUST	90.02	1.96	15.49	.461	.131	.059	.245	.01	.637
NON-CA TALYST HOT EXHAUST	402.33	37.09	46.22	1.725	.416	.376	1.564	.005	.933
HOT SOAK EVAPORATIVES	.	.	34.59	1.188					4.489
DIURNAL EVAPORATIVES	.	.	29.48	.106					4.962
RUNNING EVAPORATIVES	.	.	42.51	1.46					5.517
RESTING EVAPORATIVES	.	.	19.4	.07					3.265
DIESEL EXHAUST	128.07	201.46	20.98	.478	.045	1.756	3.514	.002	
ON-ROAD MOTOR VEHICLES - Subtotal	3603.59	658.65	433.7	12.128	2.21	3.017	9.251	.221	26.195

Table 4.1. 1997 MTBE-Based California Phase 2 Reformulated Gasoline (CaRFG)
(continued)

	South Coast Air Basin Emissions			Tons/Day					27-Oct-99
Scenario: MTBE Summer 1997	CO	NO_X	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
OTHER MOBILE SOURCES									
AIRCRAFT	87.08	15.13	15.56	.438	.312	.776	2.482		.008
TRAINS	5.02	31.38	2.08	.047	.004	.174	.348	.	
SHIPS AND COMMERCIAL BOATS	4.49	40.81	5.17	.12	.012	.417	.836	.001	.002
RECREATIONAL BOATS	246.18	2.15	41.74	1.554	.374	.359	1.446	.005	.837
OFF-ROAD RECREATIONAL VEHICLES	70.65	.41	9.4	.351	.085	.076	.318	.001	.19
COMMERCIAL/INDUSTRIAL MOBILE EQUIPMENT	885.	152.65	38.92	.88	.157	1.506	4.187	.003	.27
FARM EQUIPMENT	7.15	2.7	.51	.014	.002	.029	.061	.	.004
OTHER MOBILE SOURCES - Subtotal	1305.57	245.23	113.37	3.404	.946	3.337	9.679	.009	1.311
MOBILE SOURCES - Subtotal	4909.16	903.89	547.08	15.532	3.156	6.354	18.93	.231	27.507
NATURAL (NON-ANTHROPOGENIC) SOURCES									
NATURAL SOURCES									
WILDFIRES	170.39	2.6	9.41		.14				
NATURAL SOURCES - Subtotal	170.39	2.6	9.41		.14				
NATURAL (NON-ANTHROPOGENIC) SOURCES - Subtotal	170.39	2.6	9.41		.14				
ALL SOURCES - Total	5439.59	1083.09	1036.83	17.826	3.46	6.783	21.709	33.552	31.154

Table 4.2. 2003 MTBE-Based CaRFG

South Coast Air Basin Emissions Tons/Day 27-Oct-99

Scenario: MTBE Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
STATIONARY SOURCES									
FUEL COMBUSTION									
ELECTRIC UTILITIES	1.71	6.51	.39	.027	.	.005	.064	.	.
COGENERATION	2.81	5.71	.61	.007	.	.002	.053	.	.
OIL AND GAS PRODUCTION (COMBUSTION)	1.57	7.9	.81	.031	.	.002	.095	.	.
PETROLEUM REFINING (COMBUSTION)	8.56	7.73	1.4	.02	.002	.002	.139	.	.004
MANUFACTURING AND INDUSTRIAL	17.39	38.74	5.43	.244	.004	.072	.701	.	.003
FOOD AND AGRICULTURAL PROCESSING	.48	.9	.21	.017	.	.	.035	.	.
SERVICE AND COMMERCIAL	14.06	21.83	3.72	.117	.002	.048	.427	.	.002
OTHER (FUEL COMBUSTION)	4.41	1.85	.64	.018	.004	.004	.033	.	.008
FUEL COMBUSTION - Subtotal	51.	91.17	13.21	.481	.012	.136	1.547	.	.016
WASTE DISPOSAL									
SEWAGE TREATMENT	.03	.	.07	.	.	.	.006	.	.
LANDFILLS	.6	.59	1.35	.	.	.	.048	.	.
INCINERATORS	.13	.34	.02	.007	.	.	.	.	.
OTHER (WASTE DISPOSAL)	.	.01	.8	.	.	.	.	.	.
WASTE DISPOSAL - Subtotal	.77	.95	2.24	.007	.	.	.055	.	.
CLEANING AND SURFACE COATINGS									
LAUNDERING	.	.01	.71	.	.	.	.	.	.
DEGREASING	.	.	99.98	.	.	.	.	.	.
COATINGS AND RELATED PROCESS SOLVENTS	.26	.42	96.4	.071	.	.	.	1.771	.001
PRINTING	.02	.08	5.08	.	.	.	.	.643	.
OTHER (CLEANING AND SURFACE COATINGS)	.	.	12.08	.002	.	.	.	.003	.
CLEANING AND SURFACE COATINGS - Subtotal	.29	.51	214.26	.074	.	.	.	2.417	.001
PETROLEUM PRODUCTION AND MARKETING									
OIL AND GAS PRODUCTION	.02	.06	10.76	.165	.	.	.	.	.001
PETROLEUM REFINING	6.33	5.32	8.03	.112	.	.	.014	.	.136
PETROLEUM MARKETING	.09	.	24.1	.154	.	.	.	.	3.245
OTHER (PETROLEUM PRODUCTION AND MARKETING)	.05	.01	.2	.005	.	.	.	.	.001
PETROLEUM PRODUCTION AND MARKETING - Subtotal	6.5	5.39	43.09	.436	.	.	.014	.	3.384
INDUSTRIAL PROCESSES									
CHEMICAL	.04	.54	17.19	.001	.	.	.	.001	.
FOOD AND AGRICULTURE	.22	.11	3.28	.	.	.	.	1.091	.
MINERAL PROCESSES	2.84	6.49	.65	.	.	.	.	.	.
METAL PROCESSES	1.96	.75	.75	.	.	.	.	.	.
WOOD AND PAPER	.	.	.04	.	.	.	.	.	.
GLASS AND RELATED PRODUCTS	.	.26	.03	.	.	.	.	.	.

OTHER (INDUSTRIAL PROCESSES)	1.67	.94	2.94	.	.	.	.357	.	.
INDUSTRIAL PROCESSES - Subtotal	6.74	9.09	24.89	.001	.	.	.358	1.091	.
STATIONARY SOURCES - Subtotal	65.29	107.12	297.69	1.	.012	.136	1.974	3.508	3.401

Table 4.2. 2003 MTBE-Based CaRFG
(continued)

South Coast Air Basin Emissions Tons/Day 27-Oct-99

Scenario: MTBE Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
AREA-WIDE SOURCES									
SOLVENT EVAPORATION									
CONSUMER PRODUCTS	.	.	83.19	.	.	.	.028	24.1	.
ARCHITECTURAL COATINGS AND RELATED PROCESS SOLVENTS	.	.	72.77	.072	.	.	.	.27	.
PESTICIDES/FERTILIZERS	.	.	13.42	.595	.	.	.002	1.464	.
ASPHALT PAVING	.	.	.55	.	.	.	.	.	.
OTHER (SOLVENT EVAPORATION)	.	.	.19	.002	.	.	.	.	.
SOLVENT EVAPORATION - Subtotal	.	.	170.12	.67	.	.	.029	25.834	.
MISCELLANEOUS PROCESSES									
RESIDENTIAL FUEL COMBUSTION	43.99	23.68	2.95	.071	.	.187	.344	.	.
FARMING OPERATIONS	.	.	10.38	.	.	.	.	2.612	.
FIRES	8.06	.19	.56	.	.	.	.	.	.
WASTE BURNING AND DISPOSAL	30.89	1.44	2.34	.	.035	.	.	.	.
UTILITY EQUIPMENT	204.59	.41	11.91	.444	.107	.097	.403	.001	.24
OTHER (MISCELLANEOUS PROCESSES)	.05	.28	1.81	.	.	.	.	.	.
MISCELLANEOUS PROCESSES - Subtotal	287.57	26.	29.96	.515	.142	.284	.747	2.613	.24
AREA-WIDE SOURCES - Subtotal	287.57	26.	200.08	1.185	.142	.284	.776	28.448	.24
MOBILE SOURCES									
ON-ROAD MOTOR VEHICLES									
CATALYST COLD EXHAUST	757.45	71.4	82.09	2.164	.62	.349	1.152	.079	2.653
CATALYST HOT EXHAUST	1290.2	223.04	62.26	2.05	.428	.187	1.321	.053	1.509
NON-CATALYST COLD EXHAUST	27.12	.59	4.78	.142	.04	.018	.075	.003	.196
NON-CATALYST HOT EXHAUST	143.27	12.97	16.84	.628	.152	.137	.57	.002	.34
HOT SOAK EVAPORATIVES	.	.	19.83	.198	.	.	.	.	2.292
DIURNAL EVAPORATIVES	.	.	18.85	.068	.	.	.	.	3.173
RUNNING EVAPORATIVES	.	.	35.02	.35	.	.	.	.	4.048
RESTING EVAPORATIVES	.	.	10.93	.039	.	.	.	.	1.84
DIESEL EXHAUST	141.72	177.19	15.82	.36	.034	1.324	2.649	.002	.
ON-ROAD MOTOR VEHICLES - Subtotal	2359.79	485.2	266.42	6.001	1.273	2.015	5.768	.138	16.052

Table 4.2. 2003 MTBE-Based CaRFG
(continued)

Scenario: MTBE Summer 2003	South Coast Air Basin Emissions Tons/Day CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	27-Oct-99 MTBE
OTHER MOBILE SOURCES									
AIRCRAFT	92.63	17.24	16.92	.472	.343	.858	2.745	.	.008
TRAINS	4.79	30.01	1.99	.045	.004	.166	.333	.	.
SHIPS AND COMMERCIAL BOATS	4.85	44.48	5.59	.129	.013	.451	.904	.001	.002
RECREATIONAL BOATS	297.9	2.6	50.51	1.88	.453	.434	1.75	.005	1.013
OFF-ROAD RECREATIONAL VEHICLES	62.44	.46	3.84	.143	.035	.031	.13	.	.078
COMMERCIAL/INDUSTRIAL MOBILE EQUIPMENT	941.55	132.63	41.63	.947	.17	1.595	4.446	.003	.295
FARM EQUIPMENT	7.73	2.78	.56	.016	.003	.032	.068	.	.004
OTHER MOBILE SOURCES - Subtotal	1411.89	230.2	121.05	3.633	1.02	3.568	10.377	.01	1.4
MOBILE SOURCES - Subtotal	3771.68	715.39	387.47	9.634	2.293	5.583	16.144	.148	17.452
NATURAL (NON-ANTHROPOGENIC) SOURCES									
NATURAL SOURCES									
WILDFIRES	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL (NON-ANTHROPOGENIC) SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
ALL SOURCES - Total	4294.94	851.11	894.65	11.819	2.587	6.003	18.895	32.104	21.093

Table 4.3. 2003 Ethanol-Based Fully Complying Fuel (with Oxygen Content of 2.0 wt%)

South Coast Air Basin Emissions Tons/Day 27-Oct-99

Scenario: ET20 Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
STATIONARY SOURCES									
FUEL COMBUSTION									
ELECTRIC UTILITIES	1.71	6.51	.39	.027	.	.005	.064	.	
COGENERATION	2.81	5.71	.61	.007	.	.002	.053	.	
OIL AND GAS PRODUCTION (COMBUSTION)	1.57	7.9	.81	.031	.	.002	.095	.	.
PETROLEUM REFINING (COMBUSTION)	8.56	7.73	1.4	.02	.002	.003	.138	.004	
MANUFACTURING AND INDUSTRIAL	17.39	38.74	5.43	.244	.004	.072	.7	.003	.
FOOD AND AGRICULTURAL PROCESSING	.48	.9	.21	.017	.	.	.035	.	
SERVICE AND COMMERCIAL	14.06	21.83	3.72	.116	.002	.048	.427	.002	.
OTHER (FUEL COMBUSTION)	4.41	1.85	.64	.017	.004	.005	.032	.008	
FUEL COMBUSTION - Subtotal	51.	91.17	13.21	.48	.012	.137	1.545	.016	.
WASTE DISPOSAL									
SEWAGE TREATMENT	.03	.	.07	.	.	.	.006	.	
LANDFILLS	.6	.59	1.35	.	.	.	.048	.	
INCINERATORS	.13	.34	.02	.007	.	.	.	.	
OTHER (WASTE DISPOSAL)	.	.01	.8	.	.	.	.	.	
WASTE DISPOSAL - Subtotal	.77	.95	2.24	.007	.	.	.055	.	
CLEANING AND SURFACE COATINGS									
LAUNDERING	.	.01	.71						
DEGREASING	.	.	99.98						
COATINGS AND RELATED PROCESS SOLVENTS	.26	.42	96.4	.071	.	.	.	1.772	.
PRINTING	.02	.08	5.08	.	.	.	.	.643	
OTHER (CLEANING AND SURFACE COATINGS)	.	.	12.08	.002	.	.	.	.003	.
CLEANING AND SURFACE COATINGS - Subtotal	.29	.51	214.26	.074	.	.	.	2.417	.
PETROLEUM PRODUCTION AND MARKETING									
OIL AND GAS PRODUCTION	.02	.06	10.76	.165	.	.	.	.	.
PETROLEUM REFINING	6.33	5.32	8.03	.116	.	.	.014	.076	
PETROLEUM MARKETING	.09	.	24.1	.224	.	.	.	1.771	.
OTHER (PETROLEUM PRODUCTION AND MARKETING)	.05	.01	.2	.005	.	.	.	.001	
PETROLEUM PRODUCTION AND MARKETING - Subtotal	6.5	5.39	43.09	.51	.	.	.014	1.847	.
INDUSTRIAL PROCESSES									
CHEMICAL	.04	.54	17.19	.001	.	.	.	.001	
FOOD AND AGRICULTURE	.22	.11	3.28	.	.	.	.	1.091	.
MINERAL PROCESSES	2.84	6.49	.65						
METAL PROCESSES	1.96	.75	.75						
WOOD AND PAPER	.	.	.04						
GLASS AND RELATED PRODUCTS	.	.26	.03						

OTHER (INDUSTRIAL PROCESSES)	1.67	.94	2.94	.	.	.	.357	.	
INDUSTRIAL PROCESSES - Subtotal	6.74	9.09	24.89	.001	.	.	.358	1.092	.
STATIONARY SOURCES - Subtotal	65.29	107.12	297.69	1.072	.012	.137	1.972	5.373	.

Table 4.3. 2003 Ethanol-Based Fully Complying Fuel (with Oxygen Content of 2.0 wt%) (continued)

	South Coast Air Basin Emissions		Tons/Day						27-Oct-99
Scenario: ET20 Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
AREA-WIDE SOURCES									
SOLVENT EVAPORATION									
CONSUMER PRODUCTS	.	.	83.19	.	.	.	.028	24.1	.
ARCHITECTURAL COATINGS AND RELATED PROCESS SOLVENTS	.	.	72.77	.072	.	.	.	.27	.
PESTICIDES/FERTILIZERS	.	.	13.42	.595	.	.	.002	1.464	.
ASPHALT PAVING	.	.	.55						
OTHER (SOLVENT EVAPORATION)	.	.	.19	.002	.	.	.	.	.
SOLVENT EVAPORATION - Subtotal	.	.	170.12	.67	.	.	.029	25.834	.
MISCELLANEOUS PROCESSES									
RESIDENTIAL FUEL COMBUSTION	43.99	23.68	2.95	.071	.	.187	.344	.	.
FARMING OPERATIONS	.	.	10.38	.	.	.	.	2.612	.
FIRES	8.06	.19	.56						
WASTE BURNING AND DISPOSAL	30.89	1.44	2.34	.	.035	.	.	.	.
UTILITY EQUIPMENT	204.59	.41	11.88	.427	.105	.123	.379	.24	.
OTHER (MISCELLANEOUS PROCESSES)	.05	.28	1.81						
MISCELLANEOUS PROCESSES - Subtotal	287.57	26.	29.93	.497	.14	.31	.723	2.853	.
AREA-WIDE SOURCES - Subtotal	287.57	26.	200.05	1.167	.14	.31	.752	28.687	.
MOBILE SOURCES									
ON-ROAD MOTOR VEHICLES									
CATALYST COLD EXHAUST	757.45	71.4	81.36	2.069	.599	.443	1.074	2.618	.
CATALYST HOT EXHAUST	1290.2	223.04	61.93	1.943	.414	.236	1.226	1.49	.
NON-CATALYST COLD EXHAUST	27.12	.59	4.77	.136	.039	.023	.071	.155	.
NON-CATALYST HOT EXHAUST	143.27	12.97	16.8	.603	.149	.174	.536	.34	.
HOT SOAK EVAPORATIVES	.	.	19.85	.198	.	.	.	1.141	.
DIURNAL EVAPORATIVES	.	.	18.86	.151	.	.	.	1.763	.
RUNNING EVAPORATIVES	.	.	35.05	.35	.	.	.	2.015	.
RESTING EVAPORATIVES	.	.	10.93	.087	.	.	.	1.022	.
DIESEL EXHAUST	141.72	177.19	15.82	.36	.034	1.324	2.649	.002	.
ON-ROAD MOTOR VEHICLES - Subtotal	2359.79	485.2	265.36	5.9	1.235	2.2	5.556	10.546	.

Table 4.3. 2003 Ethanol-Based Fully Complying Fuel (with Oxygen Content of 2.0 wt%) (continued)

	South Coast Air Basin Emissions			Tons/Day					27-Oct-99
Scenario: ET20 Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
OTHER MOBILE SOURCES									
AIRCRAFT	92.63	17.24	16.92	.472	.343	.858	2.745	.	.008
TRAINS	4.79	30.01	1.99	.045	.004	.166	.333	.	.
SHIPS AND COMMERCIAL BOATS	4.85	44.48	5.59	.129	.013	.451	.904	.003	.
RECREATIONAL BOATS	297.9	2.6	50.4	1.805	.443	.544	1.648	1.013	.
OFF-ROAD RECREATIONAL VEHICLES	62.44	.46	3.84	.138	.034	.04	.122	.078	.
COMMERCIAL/INDUSTRIAL MOBILE EQUIPMENT	941.55	132.63	41.6	.925	.167	1.627	4.417	.297	.
FARM EQUIPMENT	7.73	2.78	.56	.015	.003	.033	.068	.004	.
OTHER MOBILE SOURCES - Subtotal	1411.89	230.2	120.89	3.53	1.007	3.719	10.237	1.394	.008
MOBILE SOURCES - Subtotal	3771.68	715.39	386.26	9.429	2.242	5.919	15.793	11.94	.008
NATURAL (NON-ANTHROPOGENIC) SOURCES									
NATURAL SOURCES									
WILDFIRES	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL (NON-ANTHROPOGENIC) SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
ALL SOURCES - Total	4294.94	851.11	893.41	11.669	2.533	6.367	18.518	45.999	.008

Table 4.4. 2003 Ethanol-Based Fully Complying Fuel (with Oxygen Content of 3.5 wt%)

	South Coast Air Basin Emissions				Tons/Day				27-Oct-99
Scenario: ET35 Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
STATIONARY SOURCES									
FUEL COMBUSTION									
ELECTRIC UTILITIES	1.71	6.51	.39	.027	.	.005	.064	.	.
COGENERATION	2.81	5.71	.61	.007	.	.002	.053	.	.
OIL AND GAS PRODUCTION (COMBUSTION)	1.57	7.9	.81	.031	.	.002	.095	.	.
PETROLEUM REFINING (COMBUSTION)	8.56	7.73	1.4	.02	.002	.003	.138	.006	.
MANUFACTURING AND INDUSTRIAL	17.39	38.74	5.43	.244	.004	.072	.7	.005	.
FOOD AND AGRICULTURAL PROCESSING	.48	.9	.21	.017	.	.	.035	.	.
SERVICE AND COMMERCIAL	14.06	21.83	3.72	.117	.002	.048	.427	.004	.
OTHER (FUEL COMBUSTION)	4.41	1.85	.64	.018	.004	.005	.032	.013	.
FUEL COMBUSTION - Subtotal	51.	91.17	13.21	.482	.012	.138	1.546	.028	.
WASTE DISPOSAL									
SEWAGE TREATMENT	.03	.	.07	.	.	.	.006	.	.
LANDFILLS	.6	.59	1.35	.	.	.	.048	.	.
INCINERATORS	.13	.34	.02	.007	.	.	.	.	.
OTHER (WASTE DISPOSAL)	.	.01	.8	.	.	.	.	.	.
WASTE DISPOSAL - Subtotal	.77	.95	2.24	.007	.	.	.055	.	.
CLEANING AND SURFACE COATING0S									
LAUNDERING	.	.01	.71	.	.	.	.	.	.
DEGREASING	.	.	99.98	.	.	.	.	.	.
COATINGS AND RELATED PROCESS SOLVENTS	.26	.42	96.4	.071	.	.	.	1.772	.
PRINTING	.02	.08	5.08	.	.	.	.	.643	.
OTHER (CLEANING AND SURFACE COATINGS)	.	.	12.08	.002	.	.	.	.003	.
CLEANING AND SURFACE COATINGS - Subtotal	.29	.51	214.26	.074	.	.	.	2.417	.
PETROLEUM PRODUCTION AND MARKETING									
OIL AND GAS PRODUCTION	.02	.06	10.76	.164	.	.	.	.	.
PETROLEUM REFINING	6.33	5.32	8.03	.108	.	.	.014	.077	.
PETROLEUM MARKETING	.09	.	24.1	.221	.	.	.	2.016	.
OTHER (PETROLEUM PRODUCTION AND MARKETING)	.05	.01	.2	.004	.	.	.	.001	.
PETROLEUM PRODUCTION AND MARKETING - Subtotal	6.5	5.39	43.09	.496	.	.	.014	2.095	.
INDUSTRIAL PROCESSES									
CHEMICAL	.04	.54	17.19	.001	.	.	.	.001	.
FOOD AND AGRICULTURE	.22	.11	3.28	.	.	.	.	1.091	.
MINERAL PROCESSES	2.84	6.49	.65	.	.	.	.	.	.
METAL PROCESSES	1.96	.75	.75	.	.	.	.	.	.
WOOD AND PAPER	.	.	.04	.	.	.	.	.	.
GLASS AND RELATED PRODUCTS	.	.26	.03	.	.	.	.	.	.

OTHER (INDUSTRIAL PROCESSES)	1.67	.94	2.94	.	.	.	.357	.	.
INDUSTRIAL PROCESSES - Subtotal	6.74	9.09	24.89	.001	.	.	.357	1.092	.
STATIONARY SOURCES - Subtotal	65.29	107.12	297.69	1.06	.012	.138	1.973	5.632	.

Table 4.4. 2003 Ethanol-Based Fully Complying Fuel (with Oxygen Content of 3.5 wt%) (continued)

	South Coast Air Basin Emissions		Tons/Day						27-Oct-99
Scenario: ET35 Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
AREA-WIDE SOURCES									
SOLVENT EVAPORATION									
CONSUMER PRODUCTS	.	.	83.19	.	.	.	.028	24.1	.
ARCHITECTURAL COATINGS AND RELATED PROCESS SOLVENTS	.	.	72.77	.072	.	.	.	.27	.
PESTICIDES/FERTILIZERS	.	.	13.42	.595	.	.	.002	1.464	.
ASPHALT PAVING	.	.	.55	.	.	.	.	.	.
OTHER (SOLVENT EVAPORATION)	.	.	.19	.002	.	.	.	.	.
SOLVENT EVAPORATION - Subtotal	.	.	170.12	.669	.	.	.029	25.834	.
MISCELLANEOUS PROCESSES									
RESIDENTIAL FUEL COMBUSTION	43.99	23.68	2.95	.071	.	.187	.344	.	.
FARMING OPERATIONS	.	.	10.38	.	.	.	.	2.596	.
FIRES	8.06	.19	.56	.	.	.	.	.	.
WASTE BURNING AND DISPOSAL	30.89	1.44	2.34	.	.035	.	.	.	.
UTILITY EQUIPMENT	193.67	.41	11.91	.446	.106	.225	.372	.418	.
OTHER (MISCELLANEOUS PROCESSES)	.05	.28	1.81	.	.	.	.	.	.
MISCELLANEOUS PROCESSES - Subtotal	276.65	26.	29.95	.516	.141	.413	.716	3.014	.
AREA-WIDE SOURCES - Subtotal	276.65	26.	200.08	1.186	.141	.413	.745	28.848	.
MOBILE SOURCES									
ON-ROAD MOTOR VEHICLES									
CATALYST COLD EXHAUST	700.64	71.4	81.81	2.124	.596	.799	1.037	4.606	.
CATALYST HOT EXHAUST	1193.4	223.04	62.23	2.053	.425	.436	1.218	2.689	.
NON-CATALYST COLD EXHAUST	25.08	.59	4.78	.142	.04	.042	.069	.273	.
NON-CATALYST HOT EXHAUST	132.52	12.97	16.83	.63	.151	.319	.526	.591	.
HOT SOAK EVAPORATIVES	.	.	19.85	.198	.	.	.	2.004	.
DIURNAL EVAPORATIVES	.	.	18.86	.151	.	.	.	1.803	.
RUNNING EVAPORATIVES	.	.	35.05	.35	.	.	.	3.54	.
RESTING EVAPORATIVES	.	.	10.93	.087	.	.	.	1.045	.
DIESEL EXHAUST	141.72	177.19	15.82	.36	.034	1.324	2.649	.002	.
ON-ROAD MOTOR VEHICLES - Subtotal	2193.44	485.2	266.15	6.096	1.245	2.919	5.499	16.553	.

Table 4.4. 2003 Ethanol-Based Fully Complying Fuel (with Oxygen Content of 3.5 wt%) (continued)

	South Coast Air Basin Emissions			Tons/Day					27-Oct-99
Scenario: ET35 Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
OTHER MOBILE SOURCES									
AIRCRAFT	92.63	17.24	16.92	.472	.343	.858	2.745	.	.008
TRAINS	4.79	30.01	1.99	.045	.004	.166	.333	.	.
SHIPS AND COMMERCIAL BOATS	4.79	44.48	5.59	.129	.013	.452	.904	.005	.
RECREATIONAL BOATS	275.59	2.6	50.49	1.885	.449	.976	1.618	1.762	.
OFF-ROAD RECREATIONAL VEHICLES	57.76	.46	3.84	.144	.034	.073	.12	.135	.
COMMERCIAL/INDUSTRIAL MOBILE EQUIPMENT	903.73	132.63	41.62	.948	.169	1.753	4.408	.515	.
FARM EQUIPMENT	7.23	2.78	.56	.016	.003	.035	.068	.007	.
OTHER MOBILE SOURCES - Subtotal	1346.52	230.2	121.02	3.64	1.015	4.312	10.196	2.424	.008
MOBILE SOURCES - Subtotal	3539.96	715.39	387.17	9.736	2.26	7.231	15.694	18.976	.008
NATURAL (NON-ANTHROPOGENIC) SOURCES									
NATURAL SOURCES									
WILDFIRES	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL (NON-ANTHROPOGENIC) SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
ALL SOURCES - Total	4052.3	851.11	894.35	11.982	2.553	7.781	18.412	53.456	.008

Table 4.5. 2003 Non-Oxygenated Fully Complying Fuel

South Coast Air Basin Emissions Tons/Day 27-Oct-99

Scenario: UNOX Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
STATIONARY SOURCES									
FUEL COMBUSTION									
ELECTRIC UTILITIES	1.71	6.51	.39	.027	.	.005	.064	.	
COGENERATION	2.81	5.71	.61	.007	.	.002	.053	.	
OIL AND GAS PRODUCTION (COMBUSTION)	1.57	7.9	.81	.031	.	.002	.095	.	.
PETROLEUM REFINING (COMBUSTION)	8.56	7.73	1.39	.02	.002	.002	.138	.	
MANUFACTURING AND INDUSTRIAL	17.39	38.74	5.43	.244	.004	.072	.7	.	.
FOOD AND AGRICULTURAL PROCESSING	.48	.9	.21	.017	.	.	.035	.	
SERVICE AND COMMERCIAL	14.06	21.83	3.72	.116	.002	.048	.426	.	.
OTHER (FUEL COMBUSTION)	4.41	1.85	.64	.016	.004	.004	.031	.	
FUEL COMBUSTION - Subtotal	51.	91.17	13.21	.478	.012	.135	1.544	.	.
WASTE DISPOSAL									
SEWAGE TREATMENT	.03	.	.07	.	.	.	.006	.	
LANDFILLS	.6	.59	1.35	.	.	.	.048	.	
INCINERATORS	.13	.34	.02	.007	.	.	.	.	
OTHER (WASTE DISPOSAL)	.	.01	.8	.	.	.	.	.	
WASTE DISPOSAL - Subtotal	.77	.95	2.24	.007	.	.	.055	.	
CLEANING AND SURFACE COATINGS									
LAUNDERING	.	.01	.71						
DEGREASING	.	.	99.98						
COATINGS AND RELATED PROCESS SOLVENTS	.26	.42	96.4	.071	.	.	.	1.771	.
PRINTING	.02	.08	5.08	.	.	.	.	.643	
OTHER (CLEANING AND SURFACE COATINGS)	.	.	12.08	.002	.	.	.	.003	.
CLEANING AND SURFACE COATINGS - Subtotal	.29	.51	214.26	.074	.	.	.	2.417	.
PETROLEUM PRODUCTION AND MARKETING									
OIL AND GAS PRODUCTION	.02	.06	10.76	.165	.	.	.	.	.
PETROLEUM REFINING	6.33	5.32	8.03	.115	.	.	.014	.	
PETROLEUM MARKETING	.09	.	24.1	.207	.	.	.	.	.
OTHER (PETROLEUM PRODUCTION AND MARKETING)	.05	.01	.2	.005	.	.	.	.	
PETROLEUM PRODUCTION AND MARKETING - Subtotal	6.5	5.39	43.09	.491	.	.	.014	.	.
INDUSTRIAL PROCESSES									
CHEMICAL	.04	.54	17.19	.001	.	.	.	.001	
FOOD AND AGRICULTURE	.22	.11	3.28	.	.	.	.	1.091	.
MINERAL PROCESSES	2.84	6.49	.65						
METAL PROCESSES	1.96	.75	.75						
WOOD AND PAPER	.	.	.04						
GLASS AND RELATED PRODUCTS	.	.26	.03						

OTHER (INDUSTRIAL PROCESSES)	1.67	.94	2.94	.	.	.	.357	.	
INDUSTRIAL PROCESSES - Subtotal	6.74	9.09	24.89	.001	.	.	.358	1.091	.
STATIONARY SOURCES - Subtotal	65.29	107.12	297.68	1.052	.012	.135	1.971	3.508	.

Table 4.5. 2003 Non-Oxygenated Fully Complying Fuel
(continued)

	South Coast Air Basin Emissions		Tons/Day						27-Oct-99
Scenario: UNOX Summer 2003	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
AREA-WIDE SOURCES									
SOLVENT EVAPORATION									
CONSUMER PRODUCTS	.	.	83.19	.	.	.	.028	24.1	.
ARCHITECTURAL COATINGS AND RELATED PROCESS SOLVENTS	.	.	72.77	.072	.	.	.	.27	.
PESTICIDES/FERTILIZERS	.	.	13.42	.595	.	.	.002	1.464	.
ASPHALT PAVING	.	.	.55						
OTHER (SOLVENT EVAPORATION)	.	.	.19	.002	.	.	.	.	.
SOLVENT EVAPORATION - Subtotal	.	.	170.12	.67	.	.	.029	25.834	.
MISCELLANEOUS PROCESSES									
RESIDENTIAL FUEL COMBUSTION	43.99	23.68	2.95	.071	.	.187	.344	.	.
FARMING OPERATIONS	.	.	10.38	.	.	.	.	2.612	.
FIRES	8.06	.19	.56						
WASTE BURNING AND DISPOSAL	30.89	1.44	2.34	.	.035	.	.	.	.
UTILITY EQUIPMENT	211.87	.41	11.86	.391	.105	.092	.359	.	.
OTHER (MISCELLANEOUS PROCESSES)	.05	.28	1.81						
MISCELLANEOUS PROCESSES - Subtotal	294.85	26.	29.9	.462	.14	.279	.703	2.612	.
AREA-WIDE SOURCES - Subtotal	294.85	26.	200.03	1.131	.14	.279	.732	28.446	.
MOBILE SOURCES									
ON-ROAD MOTOR VEHICLES									
CATALYST COLD EXHAUST	795.32	71.4	81.36	1.897	.599	.332	1.018	.	.
CATALYST HOT EXHAUST	1354.7	223.04	61.5	1.777	.414	.176	1.159	.	.
NON-CATALYST COLD EXHAUST	28.47	.59	4.75	.125	.039	.017	.067	.	.
NON-CATALYST HOT EXHAUST	150.43	12.97	16.76	.553	.149	.13	.507	.	.
HOT SOAK EVAPORATIVES	.	.	19.83	.198	.	.	.	.	.
DIURNAL EVAPORATIVES	.	.	18.85	.13	.	.	.	.	.
RUNNING EVAPORATIVES	.	.	35.02	.35	.	.	.	.	.
RESTING EVAPORATIVES	.	.	10.93	.075	.	.	.	.	.
DIESEL EXHAUST	141.72	177.19	15.82	.36	.034	1.324	2.649	.002	.
ON-ROAD MOTOR VEHICLES - Subtotal	2470.7	485.2	264.82	5.467	1.235	1.979	5.4	.002	.

Table 4.5. 2003 Non-Oxygenated Fully Complying Fuel (continued)

Scenario: UNOX Summer 2003	South Coast Air Basin Emissions Tons/Day CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	27-Oct-99 MTBE
OTHER MOBILE SOURCES									
AIRCRAFT	92.63	17.24	16.92	.472	.343	.858	2.745	.	.008
TRAINS	4.79	30.01	1.99	.045	.004	.166	.333	.	.
SHIPS AND COMMERCIAL BOATS	4.89	44.48	5.59	.129	.013	.451	.904	.001	.
RECREATIONAL BOATS	312.78	2.6	50.28	1.655	.443	.414	1.563	.	.
OFF-ROAD RECREATIONAL VEHICLES	65.56	.46	3.83	.126	.034	.03	.116	.	.
COMMERCIAL/INDUSTRIAL MOBILE EQUIPMENT	966.76	132.63	41.56	.881	.167	1.589	4.392	.002	.
FARM EQUIPMENT	8.06	2.78	.56	.015	.003	.032	.068	.	.
OTHER MOBILE SOURCES - Subtotal	1455.47	230.2	120.73	3.324	1.007	3.54	10.12	.003	.008
MOBILE SOURCES - Subtotal	3926.16	715.39	385.55	8.791	2.242	5.519	15.52	.004	.008
NATURAL (NON-ANTHROPOGENIC) SOURCES									
NATURAL SOURCES									
WILDFIRES	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
NATURAL (NON-ANTHROPOGENIC) SOURCES - Subtotal	170.39	2.6	9.41	.	.14	.	.	.	.
ALL SOURCES - Total	4456.7	851.11	892.67	10.974	2.533	5.933	18.223	31.959	.008

Table 4.6. Emission Inventory Data of Selected Compounds in 1997 Baseline and 2003 Scenarios for the SoCAB (tons/day)

Compounds	1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
Toluene	**77.54**	**61.93**	**59.35**	**60.56**	**58.31**
***m*&*p*-Xylene**	**28.90**	**18.72**	**16.92**	**17.72**	**16.22**
***o*-Xylene**	**12.33**	**9.30**	**8.66**	**8.93**	**8.39**
***n*-Hexane**	**22.82**	**19.94**	**19.11**	**19.42**	**20.11**
Isobutene	**14.66**	**10.01**	**5.12**	**6.65**	**5.08**
Total Alkylates[a]	**277.00**	**260.91**	**296.65**	**274.36**	**302.68**

[a]C_6+ branched alkanes and cycloalkanes.

A-4.2. Gridded Emission Inventories

The photochemical modeling was performed for the Southern California Air Quality Study (SCAQS) grid region which is the inner grid shown in Figure 4.1. This region is somewhat larger than the South Coast Air Basin. As a result, there are about 10 to 40% more emissions in the modeling region than the Air Basin depending on the year and pollutant.

The 1997 and 2003 baseline MTBE gridded inventories were developed using ARB countywide inventory estimates for ozone precursors (CO, NO_X, and TOG). All countywide area source emissions were gridded using the same area source surrogates used to grid the 1997 Southern California Ozone Study (SCOS97-NARSTO) gridded inventory (SAI, 1997). Both the spatial and temporal distributions for 1997 and 2003 for each area source category are the same for each county as in the SCOS97-NARSTO gridded inventory.

Vegetative emissions used in the 1997 SCAQMD SIP update modeling were incorporated into the ARB area source emissions to complete the area source inventory and were assumed constant for all simulations. All the area source emissions are modeled as surface sources.

All other emissions sources are contained in the ARB point source emission inventory and have associated UTM coordinates. Emissions for these sources are allocated to the proper grid cells and are also modeled as surface sources unless there are associated stack records, in which case the point source is modeled as an elevated source with calculated plume rise.

The ozone precursor inventory contains estimates of CO, NO_X (as NO_2), and TOG. Both NO_X and TOG emissions must be resolved to individual chemical species before processing further to SAPRC97 model species. NO_X emissions are assumed to be 88% NO, 10% NO_2 , and 2% HONO. TOG is resolved to chemical species through the use of organic gas species profiles. Species profiles for all gasoline-related sources have been discussed in Section A-3 and vary with each alternate gasoline. Species profiles for all other organic gas emission sources are constant for all simulations.

Emission totals within the modeling region for ozone precursors are shown in Table 4.7, for the MTBE gasoline scenarios for 1997 and 2003. NO_X and TOG emissions are constant for all 2003 scenarios. ROG emissions vary only slightly between the 2003 scenarios due to minor variations in methane emissions estimated to occur in vehicle exhaust. Motor vehicle CO emissions are the same for the MTBE and ethanol 2 wt% oxygen scenarios. Motor vehicle CO emissions are increased by 5% for the non-oxgenated gasoline scenario and reduced by 7.5% for the ethanol 3.5 wt% oxygen scenario (relative to the MTBE fleet emissions).

Table 4.7. CO, NO_X, and ROG Emissions for the SCAQS Modeling Region

(CO is for MTBE Scenarios)

YEAR	CO (tons/day)	NO_X (tons/day)	ROG (tons/day)
1997	**6,400**	**1,300**	**2,100**
2003	**5,000**	**1,050**	**1,900**

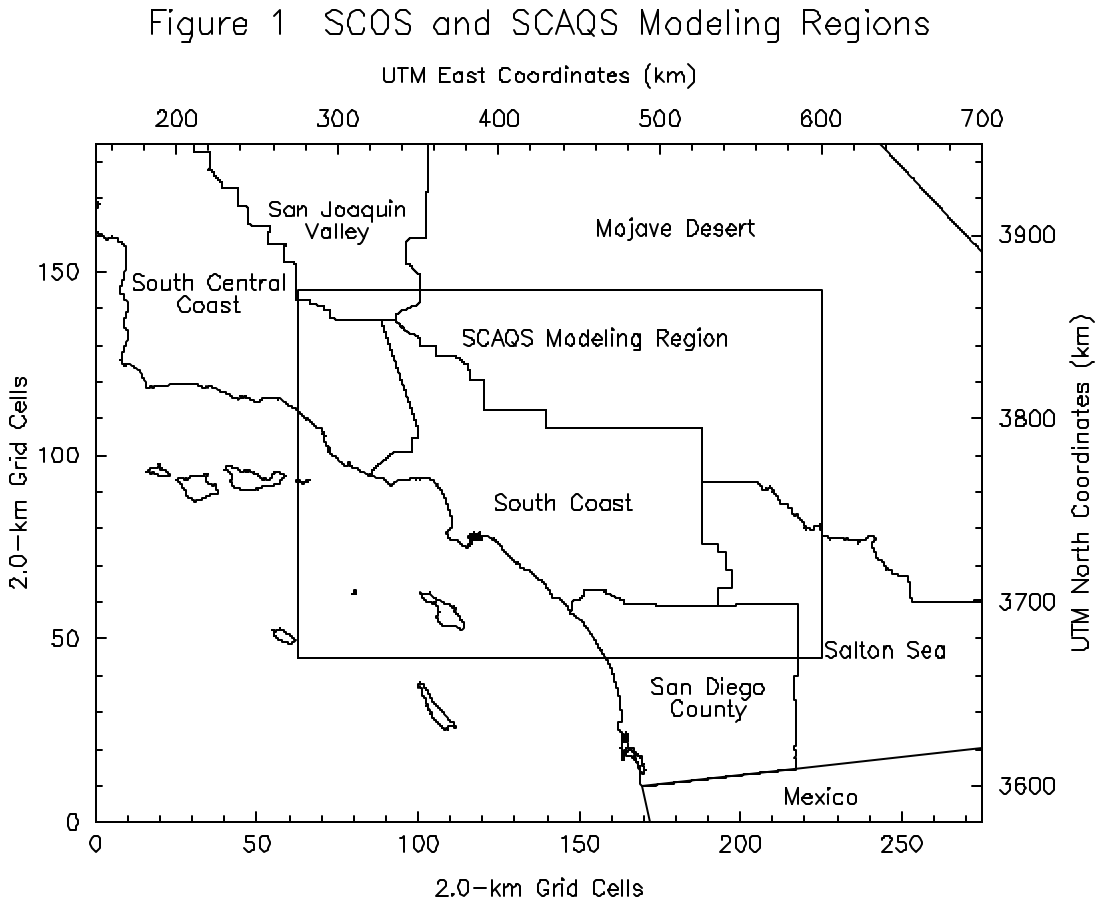


Figure 4.1. SCOS97-NARSTO and SCAQS Modeling Regions

The change in total emissions for a given pollutant from 1997 to 2003 may be different for the South Coast Air Basin than the modeling region. Both growth rates and emission controls are different inside and outside the Air Basin. For all scenarios, the same organic gas speciation profiles were used consistently throughout the modeling region.

All organic gas emission categories associated with gasoline combustion or evaporation are speciated with the gasoline specific profiles discussed in Section A-2. Emission sources that were speciated with gasoline specific profiles include gasoline marketing, distribution, storage, on and off-road mobile sources, and utility equipment. Besides the change in CO emissions discussed above, the only significant change between 2003 simulations is from the changing gasoline composition.

The organic gas speciation process results in emission estimates for over 450 separate compounds. The modeling is done with a more consolidated set of compounds. While this detailed inventory is available, it is easier to understand in terms of the SAPRC97 model species. The mechanism used in this study, which we refer to as the SAPRC97 toxics

mechanism, includes several compounds not modeled explicitly in the base SAPRC97 mechanism. Organic gas emissions are partitioned into nine important lumped organic gas model species and seventeen explicit compounds as shown in Table 4.8.

The photochemical model requires a surface-level emission file and an elevated emission file. The surface emission file contains all the organic gas emissions from gasoline related sources. The majority of elevated sources are NO_X emissions from large boilers. The SCAQS region surface emission totals for each of the above model species are shown in Table 4.9.

Table 4.8. SAPRC97 Toxic Mechanism Model Species

Explicit Species	Lumped species
ACET – acetone	**ALK1 – lower alkanes**
MEK – methyl ethyl ketone	**ALK2 – higher alkanes**
BALD – benzaldehyde	**ARO1 – lower aromatics**
GLY – glyoxal	**ARO2 – higher aromatics**
MGLYOX – methylglyoxal	**OLE1 – external alkenes**
CH4 – methane	**OLE2 – internal alkenes**
ETHE – ethene	**OLE3 – biogenic alkenes**
ISOP – isoprene	**RCHO – higher aldehydes**
BUTD – 1,3-butadiene	**CRES – cresols**
C6H6 – benzene	
PDCB – *p*-dichlorobenzene	
DICM – dichloromethane	
PERC – perchloroethylene	
FORM – formaldehyde	
ALD – acetaldehyde	
ETOH – ethanol	
MTBE –methyl *tertiary*-butyl ether	

Table 4.9. SCAQS Region Emission Comparison (kilogram moles/day)

Species	1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
CO	205,065.4	160,157.0	160,157.0	140,408.4	166,739.9
NO	21,704.8	17,445.8	17,350.9	17,350.9	17,350.9
NO2	2,466.3	1,982.4	1,971.6	1,971.6	1,971.6
HONO	480.2	386.0	383.9	383.9	383.9
RCHO	94.1	81.0	79.6	80.8	79.4
BALD	17.7	13.4	12.7	13.4	12.6
ACET	320.9	305.2	303.9	304.6	303.9
MEK	169.1	167.9	167.7	167.9	167.6
CRES	0.4	0.4	0.4	0.4	0.4
GLY	1.0	1.2	1.2	1.2	1.2
MGLY	0.7	0.8	0.8	0.8	0.8
CH4	30,105.7	29,804.7	29,777.3	29,857.4	29,769.8
ETHE	1,947.2	1,548.0	1,489.7	1,544.6	1,479.8
ISOP	1,118.2	1,114.5	1,114.4	1,114.7	1,114.1
BUTD	88.7	70.3	69.2	69.6	69.2
C6H6	253.5	170.2	161.7	172.2	158.3
PDCB	13.1	12.6	12.6	12.6	12.6
DICM	33.5	37.3	37.3	37.3	37.3
PERC	109.7	128.9	128.9	128.9	128.9
FORM	663.6	556.7	535.0	539.7	533.0
ALD	139.6	119.2	120.5	162.6	117.6
ETOH	778.4	757.6	1,080.0	1,256.6	754.2
MTBE	375.3	255.5	0.0	0.0	0.0
ALK1	4,679.7	3,993.8	3,875.7	3,881.5	4,176.8
ALK2	2,134.2	2,066.1	2,327.6	2,165.7	2,329.8
ARO1	1,009.5	788.4	750.7	766.9	733.1
ARO2	790.0	597.3	554.8	571.4	536.1
OLE1	1,030.0	779.2	661.6	708.7	657.2
OLE2	254.1	181.6	164.4	169.3	168.8
OLE3	561.2	561.0	561.0	561.0	561.0

A-5. Emission Testing

The availability of both ethanol-blended and non-oxygenated commercial CaRFG gasolines presented the opportunity to provide a reality check on the organic gas emission profiles developed in Section A-2. Because of the limited time available to conduct the ethanol fate and transport analysis, we were not able to test a fully representative number of vehicle not conduct tests of diurnal or running loss evaporative emissions.

A-5.1. Emission Testing Protocol

This section describes the protocol for the test program.

A-5.1.1. Fuels

One fuel will be a regular, unleaded, non-oxygenated gasoline. The second will be a regular gasoline blended with about 2 wt% oxygen (from ethanol). The MTBE content in this fuel should be below 1% by weight. The third gasoline will be a California commercial Phase 2 summer grade fuel with about 2 wt% oxygen (from MTBE). Complete speciation analyses for hydrocarbons, carbonyls, and alcohols will be required for all emission test samples in this program.

We obtained commercially available compliant non-MTBE gasolines in drums from fuel distributors (Chevron and Tosco in the San Francisco Bay Area). The gasolines must meet CaRFG specifications except for oxygen content. The ARB underground tank CaRFG summer grade gasoline with MTBE will be used as the third fuel. A fuel sample was obtained from each drum delivered and analyzed (complete organic gas speciation and all specifications for CaRFG). The test sequence for the two non-MTBE gasolines will be based on Table 5.1 to avoid potential biases.

A-5.1.2. Test Vehicles

One or two vehicles were selected per week from July 19 through September 15 (7 vehicles total). The desired source of vehicles is the Vehicle Surveillance Program. State vehicles with E-plates may be selected for this project when surveillance vehicles are not available. Vehicles will be selected based on the baseline FTP emission levels for hot running Bag 2 total hydrocarbon (THC). At least half of the vehicles in this project must have Bag 2 THC emissions in the range of 0.5 to 4 grams/mile. Other than this emission criterion, vehicles were randomly selected from the Surveillance Program.

Table 5.1. Fuel Test Sequence for Project 2R9905

Vehicle Number	UC Test #1	UC Test #2	UC Test #3
1	50	51	52
2	50	52	51
3	50	51	52
4	50	52	51
5	50	51	52
6	50	52	51
7	50	51	52

Fuel Code 50: California Phase 2 commercial summer grade gasoline with MTBE

Fuel Code 51: Phase 2 Chevron Non-Oxygenated gasoline

Fuel Code 52: Phase 2 Tosco 2% oxygenated gasoline with ethanol

A-5.1.3. Test Cyles

Each vehicle will undergo one cold start Unified Cycle (UC) for each fuel. Regular bag samples will be collected and analyzed at the end of the test. An extra bag will be sampled at the end of the first 100 seconds of the cold start UC test Bag 1. A modified aldehyde sample cart will be used to collect the first 100 seconds bag. Second-by-second modal data, bag results, and speciated HC bag analyses are required for all sample bags including the first 100 seconds bag. One composite background bag is acceptable for the regular 3 bag speciation analyses and the first 100 seconds sample analyses. The first 100 second sample will be labeled and reported as sample #4. Modal analyses from the dyno only provide the HC readings for the first 100 seconds; the methane readings for the first 100 seconds sample can only be based on the Pre-concentrated Direct Flame Ionization Detector (PDFID) instrument readings. The non-methane hydrocarbon (NMHC) readings for the first 100 second sample and the dilution ratio will be calculated daily by the on-site project engineer.

A-5.1.4. Vehicle Preconditioning

Test vehicles will be first classified into two groups, one group with adaptive learning and another group without adaptive learning capability. Adaptive learning is defined as vehicles with closed-loop fuel control. Cars equipped with oxygen sensors in the early 80's were the first group of vehicles with adaptive learning.

Each acceptable test vehicle with adaptive learning shall be subjected to the following preconditioning schedule:

- Drain the tank fuel
- Add 5 gallons of the correct test fuel

- Run the vehicle on the road for 50 miles (include key on/key off)
- Drain the tank fuel
- Add 3 gallons test fuel
- Start engine - one min. idle
- Drain fuel tank
- Add enough fuel to fill the tank to 40%
- Run one dummy CVS-72
- Engine off - five min. soak.
- Start engine - one min. idle
- Engine off - five min. soak
- Start engine - one min. idle
- Engine off - five min. soak
- Run one dummy CVS-72
- Cold soak the vehicle at least 12 hours, but not more than 36 hours prior to a UC or truncated UC

Each acceptable test vehicle without adaptive learning shall be subjected to the following preconditioning schedule:

- Drain the tank fuel
- Add 5 gallons of the correct test fuel
- Run the vehicle on the road for 25 miles
- Drain the tank fuel
- Add enough fuel to fill the tank 40%
- Run one dummy CVS-72
- Cold soak the vehicle at least 12 hours, but not more than 36 hours prior to a UC or truncated UC

A-5.1.5. Data Reporting and Quality Control

The test engineer will verify the test results including modal data right after each UC test. Driving violations are acceptable in this test program unless there are too many stalls (>3) that will obviously impact the results. The on-site project engineer will coordinate with MLD to obtain the preliminary GC/DYNO QC results within 2 days. Since a discrepancy exists between the modal data and composite data, the current MLD GC/DYNO QC criteria (based on composite data) may have to be adjusted to account for the difference between the modal and composite data. If the test vehicle successfully completes all three UC tests and passes the MLD QC, the test engineer will release this vehicle back to the Surveillance program.

A-5.2. Gasoline Headspace Analysis

We developed a method to sample and analyze gasoline headspace samples. The following is a brief description of the method.

- Gasoline samples are received in 1-liter metal containers and are stored in a refrigerator at approximately 0°C. One 60-ml portion of each gasoline is transferred to a 60-ml amber glass bottle and the bottles are refrigerated. Using pipettes, 10-ml of each gasoline sample is transferred from its 60-ml bottle to a 40-ml glass vial. The glass vials have plastic screw caps fitted with a Teflon lined septum. The bottles are capped immediately after introduction of the samples.
- The Mobile Source Operations Division, according to their standard procedure, makes sample bags (6-liter capacity) with Tedlar material. The bags are fitted with a QuickConnect connector and a port with a Teflon lined septum. The bags are filled with zero nitrogen to their full capacity and evacuated. This process is repeated once. Each bag is then filled with one liter of zero nitrogen.
- All sample vials and sample bags are placed inside a variable volume SHED (sealed housing for evaporative determination) maintained at 100°F for two hours. At the end of the two hours, using a gas-tight syringe, 0.3 ml of the headspace vapor is extracted from the vial and injected into the sample bag through the septum port. The bag is filled with 50-ml zero nitrogen through this port and another four liters of zero nitrogen through the QuickConnect. The bags are kept at room temperature for two hours before gas chromatography analysis.
- A gas chromatograph equipped with a flame ionization detector using standard operating procedures MLD 102 for the light-end hydrocarbons and MLD 103 for the mid-range hydrocarbons is used to analyze the samples. Both these methods are currently available on the ARB web site (http://www.arb.ca.gov/testmeth/testmeth.htm) under the mobile source programs, Low Emission Vehicle II, non-methane organic gas test procedures, attachment M to the recent regulatory action as procedures 1002 and 1003.
- The above procedures are also used to analyze motor vehicle exhaust and evaporative emissions along with the alcohol and carbonyl test methods, numbers 1001 and 1004 respectively.

A-5.3. Vehicle and Fuel Selection Processes

A-5.3.1. Vehicle Selection Process

This test program was targeted for testing at least five vehicles within two months. In order to obtain a representative fleet from a small number of vehicles, this program focused on vehicles with significant impacts on the mass emissions. The 1996-97 emission inventory data showed that 30% of the entire fleet was responsible for 80% of the total hydrocarbon (THC) emissions. These mid-range emission vehicles were selected based on the following criteria:

Any vehicles with the FTP Bag 2 THC emissions in the range of 0.5 to 4 grams/mile. At least 50% of the test vehicles in this program are required to meet the criterion.

Seven vehicles were completed in this test program at the end of September. Five vehicles were randomly selected from the Vehicle Surveillance program. The two other vehicles were selected from the State vehicles with E plates. The average odometer reading for the seven vehicles is about 101,000 miles. The average model year for the seven vehicles is 81. Four of the seven test vehicles meet the emission criteria set for this program. The average FTP Bag 2 THC emissions is 1.07 gm/mile. A description of each vehicle is presented in Table 5.3.

A-5.3.2. Fuel Selection Process

The original test plan only requested two fuels to be tested in each vehicle, one is the Chevron non-oxygenated gasoline and the other is the Tosco 2%-oxygenated gasoline with ethanol. Ten barrels of each fuel were obtained from refineries located in northern California. ARB proposed to include the commercial Phase 2 gasoline with MTBE in the program. Therefore, all seven vehicles in this test program were tested with three different fuels by a random order within each vehicle. In summary, the three fuels are as follows:

- Chevron Non-Oxygenated Gasoline
- Tosco 2% Oxygenated Gasoline with Ethanol
- ARB Commercial Phase 2 gasoline with MTBE.

At least two fuel samples were taken from each barrel when it is opened. All fuel samples were analyzed in the ARB fuel analysis laboratory. ARB chemists check fuel parameters in compliance with Phase 2 gasoline specifications as well as detailed hydrocarbon analysis (speciation) for each fuel sample. The fuel analysis data are summarized in the following table.

Table 5.2. Summary of Fuel Properties

Sample I.D.	EtOH (wt%)	MTBE (wt%)	Benzene (vol%)	Total Aromatics (vol%)	RVP psi	T50 (deg F)	T90 (deg F)	Sulfur (ppm)	Olefins (vol%)
Fuel 50	**0.00**	**10.67**	**0.57**	**23.9**	**6.79**	**201.0**	**311.0**	**14.00**	**3.60**
Fuel 51	**0.00**	**0.00**	**0.16**	**25.0**	**6.71**	**202.1**	**303.2**	**29.20**	**3.43**
Fuel 52	**5.88**	**0.00**	**0.42**	**28.0**	**6.88**	**203.8**	**316.4**	**1.22**	**0.21**

Fuel 50 **Commercial Phase 2 gasoline with MTBE**

Fuel 51 **Chevron Phase 2 non-oxygenated gasoline**

Fuel 52 **Tosco Phase 2 oxygenated gasoline with ethanol**

.

Table 5.3. Description of Vehicles

Project	2R9905	2R9905	2R9905	2R9905	2R9905	2R9905	2R9905
Vehicle Number	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Model Year	76	75	92	79	80	90	76
Manufacturer	General Motor	Mercedes	Ford	General Motor	Honda	General Motor	Ford
Division	Oldsmobile	Mercedes	Ford	Chevolet	Honda	Buick	Ford
Model Year	Delta88 Royale	450 SEL	Tempo GS	Malibu	Accord LX	Lesabre	Granada
Bag 2 FTP HC (g/mile)	1.535	1.708	0.015	0.204	0.509	0.016	3.942
Odometer (mile)	136660	150623	30151	153643	76095	57870	101020
Cylinder	8	8	4	6	4	6	8
Displacement (liter)	5.736	4.523	2.294	3.785	1.753	3.786	4.949
Drive	2R	2R	2F	2R	2F	2F	2R
Vehicle Class	Passenger Car	Passenger Car	Passenger Car	Passenger Car	Passenger Car	Passenger Car	Passenger Car
Transmission	Automatic 3 speed	Automatic 3 speed	Automatic 3 speed	Automatic 3 speed	Automatic 3 speed	Automatic 4 speed	Automatic 3 speed
Exhaust Gas Recirculation	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Oxygen Sensor	No	No	Yes	No	No	Yes	No
Fuel Injection	Carburetor	Electronic Multipoint	Electronic Multipoint	Carburetor	Carburetor	Electronic Multipoint	Carburetor
Reactor	Oxidizing Catalyst	Oxidizing Catalyst	Three-Way Catalyst Double Bed Closed Loop	Oxidizing Catalyst	Oxidizing Catalyst	Three-Way Catalyst Single Bed Closed Loop	Oxidizing Catalyst

A-5.4. Mass Emission Test Results

Table 5.4 summarizes the test results for the seven vehicles for carbon monoxide, oxides of nitrogen and non-methane hydrocarbons.

Table 5.4. Exhaust Emission Test Results (g/mi)

Vehicle	No. of	Test	Test	CO		NOx		NMHC	
Number	Tests	Type	Fuel	Bag2	Bag1-Bag3	Bag2	Bag1-Bag3[a]	Bag2	Bag1-Bag3
1	1	FTP	MTBE	36.566	28.324	0.964	0.000	1.367	1.391
2	1	FTP	MTBE	5.848	27.157	1.778	0.000	1.615	0.640
3	1	FTP	MTBE	0.635	3.647	0.105	0.367	0.004	0.423
4	1	FTP	MTBE	0.476	10.706	0.535	0.000	0.082	1.349
5	1	FTP	MTBE	7.745	5.396	2.059	0.028	0.445	0.829
1	1	UC	MTBE	33.870	21.371	2.012	0.618	0.900	3.879
1	1	UC	NonOxy	46.804	119.311	1.954	0.186	1.250	6.105
1	1	UC	Etoh	21.163	87.399	2.175	0.000	0.783	3.886
2	1	UC	MTBE	2.366	88.620	2.646	0.054	0.359	1.692
2	1	UC	NonOxy	4.784	98.584	2.985	0.000	1.840	3.038
3	1	UC	MTBE	3.542	14.679	0.342	0.796	0.013	1.552
3	2	UC	NonOxy	4.419	17.324	0.289	1.112	0.019	1.453
3	1	UC	Etoh	4.419	17.696	0.225	1.115	0.016	1.692
4	1	UC	MTBE	9.613	36.799	1.560	0.191	0.307	3.740
4	2	UC	NonOxy	42.774	57.301	0.246	0.401	1.064	6.705
4	1	UC	Etoh	15.524	43.944	0.454	0.368	0.471	4.243
5	1	UC	MTBE	32.635	19.897	2.239	0.796	1.291	5.833
5	2	UC	NonOxy	32.104	38.950	2.304	1.057	1.103	5.860
5	1	UC	Etoh	10.537	26.390	2.098	1.169	0.505	3.714
6	1	UC	NonOxy	2.202	9.451	0.143	0.518	0.014	1.570
6	1	UC	Etoh	4.156	39.009	0.128	0.519	0.018	2.038
7	1	UC	NonOxy	40.861	61.622	1.878	3.142	1.367	6.326
7	1	UC	Etoh	38.393	47.693	2.216	0.000	1.367	6.878

a: Negative values of bag1-bag3 set to zero.

Bag2 represents hot stablized emissions.

Bag1 minus Bag3 represents start emissions.

FTP: Federal Test Procedure.

UC: Unified Cycle.

Ethanol and MTBE fuels are 2.0 wt% oxygen; NonOxy fuel is non-oxygenated fuel (0 wt% oxygen) .

A-5.5. Organic Species Test Results

Full speciation was conducted on the liquid gasoline, headspace, and exhaust emissions. Summarized results are presented in Figure 5.1 through Figure 5.4 and Table 5.5 through Table 5.8. Complete speciation details for all species for each barrel of gasoline and each vehicle is included in Attachment A2.

Figure 5.1. Liquid Gasoline Organic Gas Species Test Results

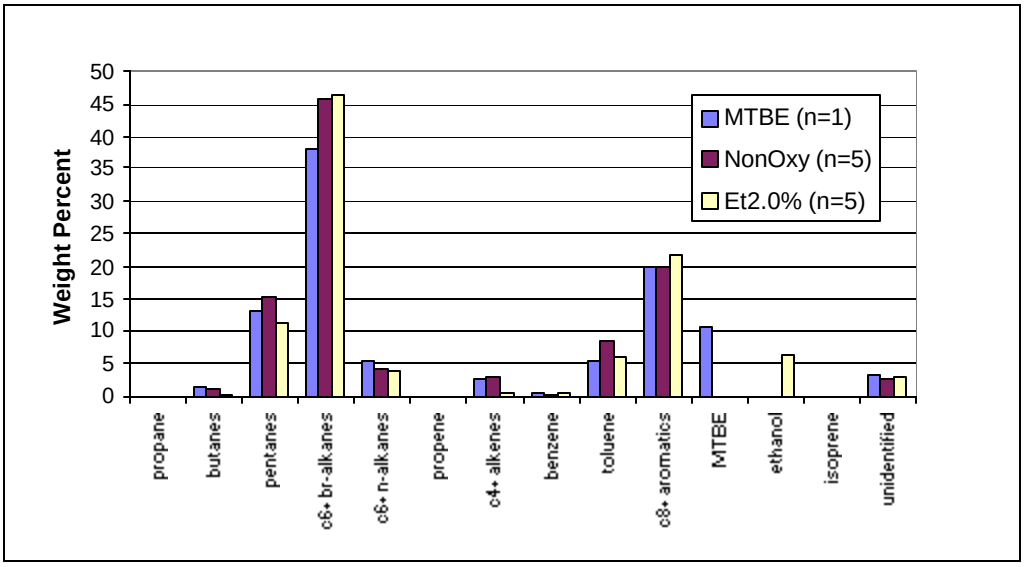


Table 5.5. Liquid Gasoline Organic Gas Species Test Results (wt%)

Group	MTBE (n=1)	NonOxy (n=5)		Et2.0% (n=5)	
Name	Mean	Mean	COV	Mean	COV
Propane	0.01	0.00	n/a	0.00	7%
Butanes	1.14	0.94	6%	0.41	2%
Pentanes	12.82	15.29	3%	11.26	2%
C6+ br-alkanes	37.83	45.50	2%	46.27	2%
C6+ n-alkanes	5.26	4.23	1%	3.78	0%
Propene	0.00	0.00	20%	0.00	0%
C4+ alkenes	2.69	2.75	2%	0.52	10%
Benzene	0.78	0.26	2%	0.57	1%
Toluene	5.41	8.56	1%	6.17	1%
C8+ aromatics	19.88	19.94	6%	21.88	3%
MTBE	10.90	0.06	11%	0.10	1%
Ethanol	0.00			6.34	5%
Isoprene	0.01	0.00	8%	0.00	0%
Unidentified	3.29	2.49	7%	2.75	37%
TOTAL	100.00	100.03		100.05	
MIR	2.42	2.55	3%	2.51	3%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Figure 5.2. Gasoline Headspace Organic Gas Species Test Results

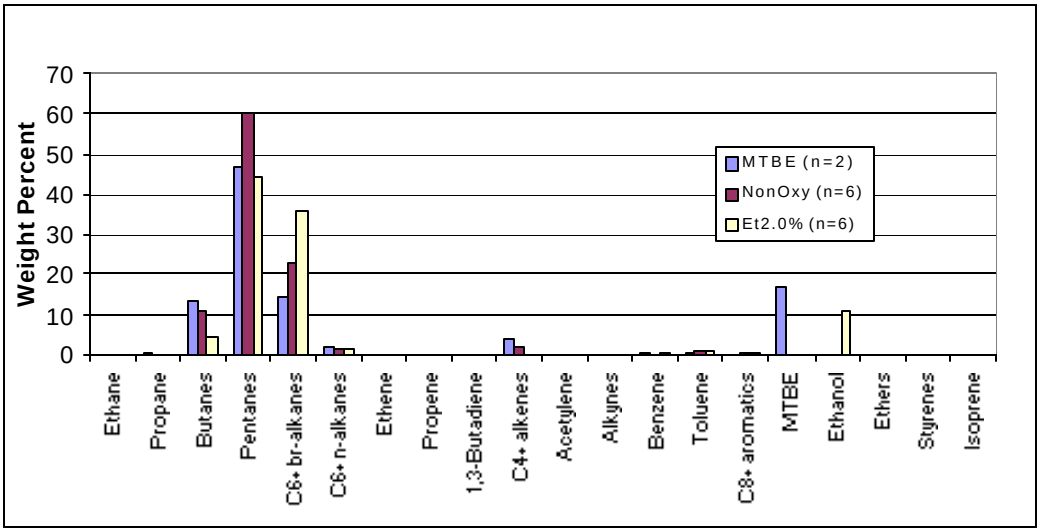


Table 5.6. Gasoline Headspace Organic Gas Species Test Results (wt%)

Group	MTBE (n=2)		NonOxy (n=6)		Et2.0% (n=6)	
Name	Mean	COV	Mean	COV	Mean	COV
Ethane	0.15	18%	0.00	n/a	0.00	n/a
Propane	0.30	28%	0.00	n/a	0.05	8%
Butanes	13.86	23%	11.01	11%	4.35	7%
Pentanes	46.93	6%	60.39	4%	44.48	5%
C6+ br-alkanes	14.21	32%	23.15	11%	35.92	2%
C6+ n-alkanes	2.07	32%	1.82	16%	1.59	6%
Ethene	0.04	17%	0.00	n/a	0.00	n/a
Propene	0.08	28%	0.00	n/a	0.00	n/a
1,3-Butadiene	0.02	141%	0.00	n/a	0.00	n/a
C4+ alkenes	4.00	2%	2.08	5%	0.26	8%
Acetylene	0.00	n/a	0.00	n/a	0.00	n/a
Alkynes	0.00	n/a	0.00	n/a	0.00	n/a
Benzene	0.45	0%	0.19	0%	0.39	0%
Toluene	0.60	62%	1.01	34%	1.18	17%
C8+ aromatics	0.22	46%	0.43	50%	0.67	37%
MTBE	17.08	3%	0.00	n/a	0.00	n/a
Ethanol	0.00	n/a	0.00	n/a	11.19	11%
Ethers	0.00	n/a	0.00	n/a	0.00	n/a
Styrenes	0.00	n/a	0.00	n/a	0.00	n/a
Isoprene	0.01	141%	0.00	n/a	0.00	n/a
TOTAL	100.01		100.08		100.06	
MIR	1.47	1%	1.45	3%	1.43	1%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).

Figure 5.3. Exhaust Gasoline Organic Gas Species Test Results (Hot Stabilized Emissions)

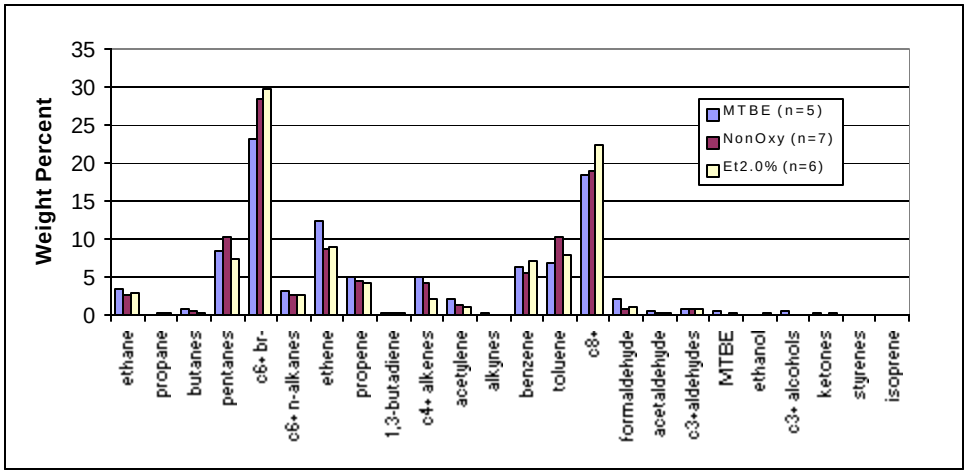


Table 5.7. Exhaust Gasoline Organic Gas Species Test Results (Hot Stabilized Emissions, wt%)

Group	MTBE (n=5)		NonOxy (n=7)		Et2.0% (n=6)	
Name	Mean	COV	Mean	COV	Mean	COV
Ethane	3.42	79%	2.56	68%	2.79	40%
Propane	0.08	76%	0.22	173%	0.35	131%
Butanes	0.66	60%	0.60	39%	0.39	31%
Pentanes	8.50	17%	10.24	19%	7.42	19%
C6+ br-alkanes	23.25	29%	28.30	17%	29.74	19%
C6+ n-alkanes	3.03	35%	2.54	20%	2.67	22%
Ethene	12.27	60%	8.63	49%	8.94	51%
Propene	4.95	51%	4.42	32%	4.10	39%
1,3-Butadiene	0.16	77%	0.23	134%	0.14	136%
C4+ alkenes	5.00	59%	4.21	47%	2.11	83%
Acetylene	2.01	77%	1.20	125%	1.05	94%
Alkynes	0.21	91%	0.07	85%	0.11	123%
Benzene	6.27	45%	5.55	46%	7.20	43%
Toluene	6.74	18%	10.37	10%	7.79	8%
C8+ aromatics	18.55	48%	18.82	31%	22.33	41%
Formaldehyde	2.19	176%	0.71	177%	0.98	137%
Acetaldehyde	0.62	167%	0.24	159%	0.38	166%
C3+aldehydes	0.74	160%	0.74	143%	0.77	138%
MTBE	0.41	32%	0.08	171%	0.24	137%
Ethanol					0.15	173%
C3+ alcohols	0.62	192%	0.06	265%	0.10	176%
Ketones	0.26	79%	0.10	101%	0.18	122%
Styrenes	0.06	62%	0.10	160%	0.07	157%
Isoprene	0.01	224%	0.02	145%		
TOTAL	100.00		100.00		100.00	
MIR	3.98	11%	3.63	9%	3.72	5%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Hot stabilized emissions are represented by Bag 2 of Unified Cycle.

Figure 5.4. Exhaust Gasoline Organic Gas Species Test Results (Start Emissions)

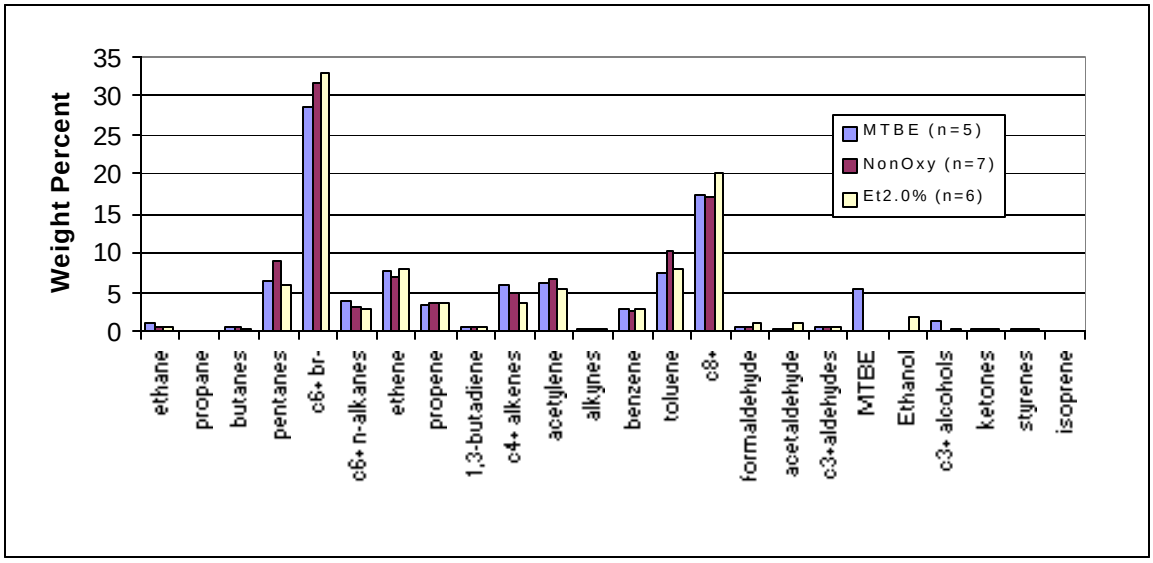


Table 5.8. Exhaust Gasoline Organic Gas Species Test Results (Start Emissions, wt%)

Group	MTBE (n=5)		NonOxy (n=7)		Et2.0% (n=6)	
Name	Mean	COV	Mean	COV	Mean	COV
Ethane	0.90	75%	0.72	49%	0.70	30%
Propane	0.07	92%	0.05	52%	0.06	52%
Butanes	0.49	54%	0.55	47%	0.32	38%
Pentanes	6.28	61%	8.96	20%	5.77	16%
C6+ br-alkanes	28.59	39%	31.69	22%	32.82	19%
C6+ n-alkanes	3.81	37%	2.98	22%	2.79	23%
Ethene	7.62	62%	7.05	34%	7.96	34%
Propene	3.43	58%	3.61	38%	3.74	32%
1,3-Butadiene	0.59	55%	0.49	47%	0.54	77%
C4+ alkenes	5.76	28%	4.89	30%	3.66	33%
Acetylene	6.05	86%	6.75	71%	5.53	58%
Alkynes	0.36	91%	0.30	82%	0.36	69%
Benzene	2.79	58%	2.32	40%	2.62	27%
Toluene	7.30	14%	10.36	7%	8.02	6%
C8+ aromatics	17.32	27%	17.01	19%	20.15	27%
Formaldehyde	0.65	78%	0.67	76%	0.84	35%
Acetaldehyde	0.28	71%	0.37	70%	0.79	33%
C3+aldehydes	0.47	55%	0.49	61%	0.56	45%
MTBE	5.49	64%	0.10	67%	0.10	61%
Ethanol			0.04	265%	1.89	66%
C3+ alcohols	1.33	42%	0.08	130%	0.22	85%
Ketones	0.24	65%	0.27	69%	0.26	37%
Styrenes	0.16	39%	0.19	36%	0.24	56%
Isoprene	0.04	118%	0.05	113%	0.07	125%
TOTAL	100.00		100.00		100.00	
MIR	3.47	19%	3.45	9%	3.72	5%

Note: COV (Coefficient of Variation) = (Standard Deviation)/(Mean)x100 (in percent).
The COVs were calculated before the mean and standard deviation were rounded.
MIR means Maximum Incremental Reactivity (g ozone/g NMOG).
Start emissions are represented by Bag 1 minus Bag 3 of Unified Cycle.

A-6. Comparison of Emission Testing with Profiles

A-6.1. Limitations of Test Program

The data obtained from testing three commercially available CaRFGs have only limited utility for evaluating the liquid gasoline compositions, headspace compositions, and exhaust emission profiles developed according to the procedures of Section A-2. The specific reactivities (overall MIRs) calculated from the test data cannot be expected to equal the reactivities of typical future MTBE-free CaRFGs and their emissions. The uncertainty about the validity of the test results stems from several factors:

- The MTBE-free gasolines have some properties that are probably atypical of future ethanol-blended CaRFGs. Most important, the sulfur content is very low (~1 ppm) in the ethanol-blended gasoline; and in the non-oxygenated gasoline it is much higher (29 ppm) than the proposed "Phase 3" flat limit for sulfur of 20 ppm (ARB, 1999a). Also, the RVP and olefinic content of the ethanol-blended gasoline were lower than is expected for future ethanol-blended CaRFGs (under the proposed variable-RVP provision). Gasolines with more reasonable values of sulfur and olefins and RVP could have substantially different compositions that did the test gasolines.
- The test vehicles as a group are aged; the mean model year among the vehicles for which the exhaust was speciated is 1981. They do not represent well the emission-control technology that is on the road today, let alone the technology in 2003. Only two have 3-way catalysts, and only three are fuel-injected. Only one is a Japanese brand.
- Several of the vehicles apparently had unstable exhaust emission rates. Many of the differences between gasolines within the same vehicle (up to a factor of five) are too large to be attributed to fuel effects; so, temporal variability in emissions may be assumed. However, we cannot estimate that variability well and separate it from the true fuel effects because no observations on the MTBE-free gasoline were replicated.
- In only four vehicles were all three test gasolines tested. For some of the vehicles, exhaust aldehydes and isobutene were not reported for some gasolines.
- Only one MTBE-blended, one ethanol-blended, and one non-oxygenated gasoline were tested. Hence, there is no information on the variability of emission measurements within a class of gasoline.
- The test data for the MTBE-free gasolines are from the Unified Cycle, whereas the modeling profiles are based on FTP data.

The headspace measurements from the test gasolines are of interest to compare with the headspace compositions used to represent diurnal emissions in the ozone modeling. Table 6.1 shows ratios of some species and groups between the headspaces and their whole gasolines. Except for the olefins, the ratios are similar for the sampled gasolines and the profiles.

Table 6.1. Headspace to Liquid Gasoline Ratios for Organic Gases

	Test Data[a]		Profiles	
	Et2.0%	NonOxy	Et2.0%	NonOxy
Ethanol	1.76		1.63	
C4+ olefins	0.49	0.76	2.1	1.6
C8+ aromatic	0.031	0.022	0.051	0.044
Toluene	0.19	0.12	0.26	0.22
Benzene	0.75	0.74	0.80	0.69
C6+ br. alkanes	0.78	0.51	0.53	0.47
Butanes	10.6	11.6	13.8	10.5
Pentanes	3.9	3.9	4.9	3.5

[a]Ratios are of means across all vehicles. Number of vehicles varies by fuel. Means exclude zeros in the data.

For start exhaust emission, Table 6.2 shows the ratios of species between the ethanol-blended and MTBE-blended gasoline and between the non-oxygenated and MTBE-blended gasoline, for the test results and for the model profiles.

Table 6.2. Ratios of Organic Gases Between Gasolines for Starts Exhaustt

	Test Data[a]		Profiles[b]	
	EtOH/MTBE	NonOxy/MTBE	EtOH/MTBE	NonOxy/MTBE
Ethanol	1.9 wt%[c]	--	3.0 wt%[c]	--
C4+ olefins	0.64	0.85	0.76	0.76
C8+ aromatics	1.16	0.98	0.91	0.91
Toluene	1.10	1.42	0.91	0.91
Benzene	0.94	0.83	0.96	0.88
C6+ br. alkanes	1.15	1.11	1.34	1.45
Butanes	0.66	1.13	0.92	0.92
Pentanes	0.92	1.54	0.91	1.0
Isobutene	0.26	0.47	0.48	0.48
Formaldehyde	1.03	0.97	0.94	0.89
Acetaldehyde	2.31	1.26	1.26	0.94

[a]Ratios are of means across all vehicles. Number of vehicles varies by gasoline. Means exclude zeros in the data.

[b]Non-catalyst.

[c]For ethanol, the entry is the content of the test emissions or profile.

As mentioned above, the design of the experiment and the variability of results do not permit an attempt to corroborate the exhaust quantitatively. However, some qualitative observations about the table may be in order.

- As in the profiles, isobutene is less plentiful in the emissions from the MTBE-free test gasolines than from the MTBE-blended test gasoline. This is expected because isobutene is a product of combustion of MTBE.
- The C_6+ branched alkanes (which include branched alkanes and cycloalkanes) are more plentiful in the emissions from the MTBE-free test gasolines than from the MTBE-blended test gasoline. This is consistent with the assumption in the profile development that each C_7 to C_9 branched alkane (but not cycloalkane) in the MTBE exhaust profiles should be increased (by 1.85 for the ethanol-blended gasoline and by 2.0 for the non-oxygenated gasoline).
- As in the profiles, the formaldehyde is slightly greater from the ethanol-blended test gasoline than from the non-oxygenated test gasoline, and the acetaldehyde is substantially greater. The ratio for acetaldehyde from the ethanol-blended test gasoline (2.31) is much higher than in the profiles. It may be due to large vehicle-to-vehicle variations in the acetaldehyde exhaust fraction (as well as temporal instability within vehicles).
- Unlike the profiles, the exhausts from the MTBE-free gasolines were higher in aromatics and olefins than was the exhaust from MTBE-blended test gasoline.

With consideration of the problems in the test design and the data variability, the test results do not contradict the model profiles.

A-7. References

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