

Appendix L

Reactivity of Motor Vehicle Emissions

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Specific reactivity is a measure of how much ozone would be produced by a unit mass of emissions, and is typically expressed as gram of ozone per gram of non-methane organic gases (NMOG). The relative reactivity is the ratio of the evaporative emission specific reactivity to the exhaust emission specific reactivity. To calculate the specific reactivity, the chemical compounds in the exhaust and evaporative emission must be identified and quantified.

Following is a discussion as to how the reactivity for each mode of emissions that are to be used the to Predictive Model were determined.

Test Programs

Although there have been numerous emission studies conducted, those that contained speciated emissions data are limited. We evaluated speciation data from five studies to determine the reactivity for each mode of evaporative emission. The studies are the ATL Phase 1/Phase 2 Study, the Auto/Oil Air Quality Improvement Program (Phase 1 and Phase 2), the Chevron Test Program, and the ARB EtOH Study. These studies provide a very robust set of speciation data for evaporative emissions. However, not all modes of evaporative emissions were measured in each study. Phase 2 of the Auto/Oil Program only measured hot soak emissions and the ARB EtOH Study dose not have running loss emission data.

Methodology

First, we calculated the average of reactivity from multiple tests for each vehicle within a study. We then calculated the average reactivity value (specific and relative) in each study across all vehicles for a particular fuel. The final reactivity values are an average of all the different fuels tested in all of the studies.

We also investigate the effect of fuel properties on the relative reactivity of evaporative emissions. We plotted the relative reactivity value for each mode of evaporative emission against the olefin, aromatic, and oxygen contents of the fuels. These plots did not show any apparent relationships between aromatic and oxygen content and the relative reactivity of evaporative emissions. However, there appears to be a relationship between the olefin content in the fuel and the relative reactivity of diurnal emissions. The relative reactivity values of diurnal emission increased at higher levels of olefin.

Most of the tests with diurnal emission data were for fuels with olefin contents less than 10 volume percent, which is the Cap Limit. We made a separate plot of the relative reactivity values for the fuels with olefin contents less than 10 percent. This plot did not show any apparent relationship between olefin contents and the relative reactivity of

diurnal emissions. Thus, we used only those data for fuels with 10 volume percent olefin or less for calculating the relative reactivity for diurnal emissions. For uniformity, we also calculated relative reactivity values for hot soak and running loss emissions using data from fuel with olefin contents less than 10 percent. There does not appear to be a relationship between the relative reactivity values of hot soak and running loss emissions and olefin content. The average relative reactivity for hot soak emissions for fuels with olefin content 10 volume percent or less is 0.87 and the relative reactivity for all fuels is 0.86. The running loss relative reactivity is the same for both methods of calculation.

Table 1 contains the average specific and relative reactivity for each mode of HC. Table 1 also presents the average reactivity value for each of the studies. The detailed data from each of the studies are presented in Appendix 1.

TABLE 1

Specific and Relative Reactivity of Emissions from Gasoline-Powered Vehicles

STUDY	AVERAGE SPECIFIC REACTIVITY				REALTIVE REACTIVITY		
	EXHAUST	EVAPORATIVE			EVAPORATIVE / EXHAUST		
		Diurnal	Hot Soak	Running loss	Diurnal	Hot Soak	Running Loss
ARB ATL PHASE1/ PAHSE 2	3.35	2.55	2.80	3.61	0.75	0.77	1.10
AUTO/OIL PHASE 1	3.21	2.09	2.82	1.61	0.67	0.85	0.51
AUTO/OIL PHASE 2	3.68		3.30			0.90	
ARB ETOH STUDY	3.52	1.71	2.51		0.50	0.73	
CHEVRON STUDY	2.97	1.46	1.96		0.50	0.67	
AVERAGE of all DATA	3.35	2.09	2.90	1.92	0.65	0.86	0.60

Table 2 shows a breakdown of the evaporative emissions from gasoline vehicles in the year 2005. The weighted-average MIR for evaporative emission has been calculated to be about 2.21 grams of ozone per grams of NMOG based the average specific reactivity and the weighted-fractions for each of the three modes of evaporative emissions. The weighted-fractions MIR for each mode of the evaporative emission and the overall average MIR are presented in Table 3.

Table 2
Breakdown of Evaporative Emissions from Gasoline-Powered Vehicles

	71 -74	75 -80	81-85	86-90	91-95	96-05	Total	Percent
Diurnal	2.3	6.8	9.6	14.2	14.9	17.4	65.1	29.8%
Hot Soak	3.4	8.4	7.8	10.4	11.5	11.1	52.6	24.0%
Running	0.7	1.9	5.1	19.2	43.3	30.8	101.0	46.2%

Table 3
Average Specific Reactivity of Evaporative Emissions

	Fraction of Inventory	Specific Reactivity	Weighted Fractions
Diurnal	30%	2.09	0.62
Hot Soak	24%	2.90	0.70
Running	46%	1.92	0.89
Average MIR			2.21