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The Effects of Oxygen-Enriched Intake Air on FFV Exhaust Emissions Using M85

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ABSTRACT

This paper presents the results of emission tests of a flexible fuel vehicle (FFV) powered by an SI engine, fueled by M85, and supplied with oxygen-enriched intake air containing nominal 21%, 23%, and 25% oxygen (by volume). Emission data were collected by following the standard federal test procedure (FTP) and U.S. Environmental Protection Agency's (EPA's) "off-cycle" test EPA-REP05. Engine-out total hydrocarbons (THCs) and unburned methanol were considerably reduced in the entire FTP cycle when the oxygen content of the intake air was either 23% or 25%. However, CO emissions did not vary appreciably, and NO_x emissions were higher. Formaldehyde emissions were reduced by about 53% in bag 1, 84% in bag 2, and 59% in bag 3 of the FTP cycle when 25% oxygen-enriched intake air was used. During the cold-phase FTP, reductions of about 42% in THCs, 40% in unburned methanol, 60% in nonmethane hydrocarbons (NMHCs), and 45% in nonmethane organic gases (NMOGs) were observed when 25% oxygen-enriched intake air was used. The corresponding NO_x emissions increased by about 78%. In general, converter-out emissions obtained were also reduced when oxygen-enriched intake air was used, but to a lesser degree. Off-cycle, bag 3 converter-out emissions were reduced when 23% oxygen-enriched intake air was used; CO emissions were reduced by about 67%, and THCs were reduced by about 52%. The FFVs operating on M85 that use 25% oxygen-enriched intake air during only the initial 127 s of the cold-phase FTP or that use 23% or 25% oxygen-enriched intake air during only the cold-phase FTP can meet (without adjusting for catalyst deterioration factors) the reactivity-adjusted NMOG, CO, NO_x, and formaldehyde emission standards of the transitional low-emission vehicle (TLEV).

INTRODUCTION

Flexible-fuel vehicles that can operate on mixtures of gasoline and methanol are being produced by various manufacturers so customers will have the flexibility to select either gasoline or M85 on the basis of price and availability. An FFV's exhaust contains a broad range of HC species as well as unburned methanol and aldehydes (primarily formaldehyde). Aldehyde emission levels are generally about 3 to 7 times higher from experimental FFVs running on methanol or M85 than running on gasoline fuel [1]. Moreover, aldehyde emissions increase as the vehicle's mileage accumulates [2]. Control of unburned methanol and formaldehyde emissions from FFVs is particularly important because of the high emissions' toxicity and photochemical reactivity. Previous studies [3,4] have clearly shown that the maximum air-quality benefit from methanol fuel can be obtained if formaldehyde is kept to very low levels.

Formaldehyde is formed by the oxidation of unburned methanol during the exhaust process, but not all the unburned methanol is converted to formaldehyde. The peak values of formaldehyde formed during methanol oxidation are higher for a deactivated catalyst than for a new catalyst. A combination of the increased partial oxidation of methanol and the decreased ability of the catalyst to oxidize formaldehyde results in higher converter-out formaldehyde emission levels as a vehicle's mileage accumulates [5]. Any increase in engine-out emissions of unburned methanol and formaldehyde can also be expected to produce more emissions at the tailpipe. Catalytic control of exhaust emissions from FFVs poses a big problem, because many catalysts tend to partially oxidize unburned methanol to formaldehyde at the temperatures typically encountered during the converter warm-up period. Thus, the present catalytic converters for FFVs must not only meet the usual requirements related to the control of gasoline-derived exhaust pollutants but have limitations with regard to the complete oxidation of unburned methanol. The various approaches typically used to minimize formaldehyde emissions are those that decrease emissions during the start-up and warm-up periods. Possible strategies include (1) decreasing engine-out unburned methanol and aldehyde emission levels, (2) increasing the warm-up rate of the engine and catalytic converter, and (3) improving the activity durability of the catalyst [5].

Several new LEV and ULEV technologies are presently being investigated to increase the warm-up rate of the converter. They include the electrically heated catalyst, exhaust gas igniter, and hydrocarbon trap [6]. Efforts are also in progress to increase the durability of the catalyst as mileage accumulates [7]. However, it is always the most desirable option if the engine itself emits lower levels of undesirable exhaust species. In this regard, oxygen-enriched combustion is a potentially attractive concept. Oxygen-enriched intake air can lead to better and more complete combustion; as a result, lower levels of THCs, unburned methanol, aldehydes, and CO are emitted in the engine's exhaust. The use of such intake air has been considered a proven technique to reduce exhaust THC and CO emissions from automotive gasoline engines [8,9]. Oxygen-enriched intake air can reduce the engine-out emissions rapidly even when the engine is cold, and it helps to minimize the converter limitations during the initial start-up and warm-up periods. The potential benefits of oxygen-enriched intake air in reducing the cold-phase THC and CO emissions from an FFV running on Indolene fuel were recently reported [10]. Despite the advantages of lower THC and CO emission levels, the higher NO_x emission level and lack of an economical on-line oxygen-enrichment system might limit the application of this technique for light-duty vehicles (LDVs). To keep NO_x emission levels low with oxygen-enriched intake air while meeting the NMHC/NMOG and CO emission standards, several application strategies were recommended [11]. Among these, application of 25% oxygen-enriched intake air during only the initial start-up and warm-up periods (first 127 s of the cold-phase FTP cycle) can meet the limit of 0.2 gram of NO_x per mile. Results obtained from FTP tests using Indolene fuel, compared with emission standards for LDVs for the year 2004 (Tier II) and with California standards, are provided in Table 1 [11]. In a separate study, attempts are also being made to reduce NO_x emissions by using monatomic nitrogen that is induced by a pulsed-arc device developed at Argonne National Laboratory [12]. The success of the oxygen-enriched combustion concept greatly depends on the availability of a compact, economical air-separation membrane able to produce the desired oxygen-enriched intake air for automotive gasoline engines. In this regard, several developmental issues, such as type of membrane material, coating thickness, fiber size, module geometry, mode of operation (vacuum, pressure, or mixed), module size, and parasitic power requirements, are currently being investigated. A prototype air-separation (oxygen) membrane that uses a new membrane material (perfluorodioxole) is being prepared for testing in a vehicle [13].

PRESENT WORK

This paper presents the results from tests of an SI-engine-powered FFV running on M85, with intake air containing nominal 21% (ambient air), 23%, and 25% oxygen by volume. Bottled oxygen was employed to increase the oxygen content of ambient air to 23% or 25% during the tests. Both the FTP-75 test and one of the EPA's newly developed off-cycle exhaust emission test (REP05) were conducted. Data collected covered mass emissions; time-resolved (second-by-second) THC, CO, and NO_x concentrations; and complete HC speciation. A portion of the time-resolved emission data for the first 127 s of the cold-phase FTP are presented to illustrate the effects of oxygen-enriched intake air. The first 127 s of the FTP includes the engine start, a 20-s idle, and the first "hill" (cycle) of the test. Detailed time-resolved emission analyses of both engine-out and converter-out emissions were made because of converter limitations during this 127-s period. Tests were designed to show whether the intake-air oxygen-enrichment technique would have any major impact on a three-way catalytic converter's performance during both open-loop and closed-loop conditions. The optimal level of oxygen enrichment and the optimal duration of its application were also examined with regard to reducing both THC and CO emissions and to keeping the NO_x level low. During the FTP cycle tests, the engine-out exhaust HC speciation was carried out only in experiments using ambient and 25% oxygen-enriched intake air. Tests with 23% oxygen-enriched intake air were not speciated. Also, exhaust HC/aldehyde speciation analyses were not performed during the off-cycle tests.

EXPERIMENTAL TEST SETUP AND PROCEDURES

OXYGEN-ENRICHMENT SYSTEM - The experimental setup was made up of the air-handling and the oxygen-supply systems, as shown in Figure 1. The air-handling system consisted of a plenum and a 300-standard cubic feet per minute (scfm) blower that continuously provided the plenum with excess air and from which the vehicle drew the intake air

Table 1. FTP converter-out emission results with oxygen-enriched air and different emissions standards for Indolene fuel

	NMHC (g/mi)		NMOG(g/mi)		CO (g/mi)		NO_x (g/mi)	
Case or Standard	Bag 1	Weighted	Bag 1	Weighted	Bag 1	Weighted	Bag 1	Weighted
Case								
(1) Ambient air (21% O_2)	0.468	0.138	0.496	0.151	4.755	1.772	0.315	0.075
(2) 25% O_2 (initial 127 s of bag 1)	0.369	0.120	0.396	0.125	3.791	1.602	0.783	0.180
(3) 23% O_2 (bag 1 only)	0.410	0.128	0.416	0.133	3.743	1.540	0.655	0.151
(4) 25% O_2 (bag 1 only)	0.329	0.111	0.338	0.117	2.633	1.367	1.497	0.303
Emission Standards at 50,000 miles								
Tier II (2004)		0.125				1.7		0.2
TLEV				0.125		3.4		0.4
LEV				0.075		3.4		0.2
ULEV				0.04		1.7		0.2

Source: Reference 11

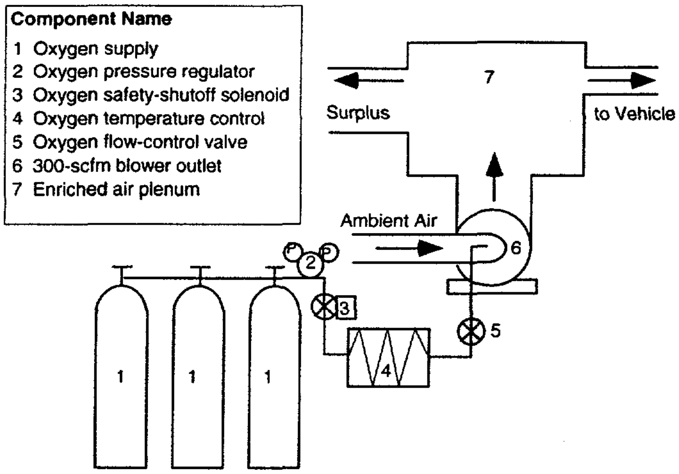

Figure 1. Diagram of oxygen-enriched system

(as required) and from which the excess air was purged. This system was designed to handle both ambient air and air enriched up to 30% with oxygen.

The oxygen-supply system consisted of 12 compressed-oxygen cylinders containing about twice the amount of oxygen required for one FTP emission test. The output pressure of the oxygen cylinders was controlled by a two-stage manual regulator. The oxygen flowed through two liquid-oxygen vaporizers and an air-to-air heat exchanger to increase the oxygen's temperature to room temperature. The heated air was then fed into the air-handling system located immediately before the blower inlet to ensure thorough mixing with ambient air. The well-mixed oxygen-enriched air was uniform in both temperature and oxygen concentration when it reached the plenum. The oxygen flow rate was controlled manually by a valve placed after the heat exchanger. Before the start of the test, the blower was turned on, and the oxygen control valves were opened and controlled to provide the desired oxygen content at the plenum.

VEHICLE MODIFICATIONS - The vehicle selected for this study was a 1993 flexible-fuel Dodge Spirit equipped with a 2.5-L port-fuel-injected engine; the vehicle had an odometer reading of 3,364 km. The vehicle was modified for tests to use oxygen-enriched air in the same manner it was used during the previous study operating on Indolene fuel [14]. To avoid drawing oxygen-enriched air through the engine crankcase, the positive crankcase ventilation (PCV) system was modified to draw intake air directly from the oxygen-enrichment system to the intake manifold. The evaporative emission control system was modified to avoid drawing oxygen-enriched air through the carbon canister. The purge line from the canister to the engine was disconnected at the canister and relocated to a port on the air filter housing. This configuration caused the engine to draw only oxygen-enriched air instead of ambient air and fuel vapors when the canister purge solenoid was activated. The fuel tank's vapor line was connected to a remote canister. The exhaust system was modified to allow use of either the OEM catalyst to obtain tailpipe emissions or a simulator converter to obtain engine-out emissions. The simulator converter did contain a briquette without a catalyst, but this was modified to give the same back-pressure as that given by an OEM catalyst.

TEST FUEL - The M85 used for these tests was supplied by BP Oil. The HC portion of the fuel was blended with methanol to yield M85. Alkylate and iso-crackate refinery streams were used for this HC blend. A sample of the HC blend used for the M85 was analyzed to determine its composition by using the PIANO test method. This analysis, along with the percentage of methanol, water, and hydrocarbons in the M85 were used to calculate the average molecular weight, hydrogen/carbon/oxygen, and density of the M85 for use in the exhaust THC emissions calculations. The PIANO HC analysis was also helpful for interpreting exhaust speciation data. The M85 was blended to the low side of the Reid vapor pressure (RVP) specifications for summer fuel (9.0 to 10.9 psi) to be as close as possible to the RVP of the Indolene (8.7 psi).

EXHAUST EMISSIONS TEST PROCEDURE - Both the FTP-75 and off-cycle exhaust emission tests were conducted in duplicate. These tests were conducted as specified in the *Code of Federal Regulations* (CFR) [15], with the exceptions given below:

1. The first test conducted with this vehicle was a preconditioning test done using a modification of the procedure adopted by the Auto/Oil Air Quality Improvement Research Program (AQIRP) [16]. This procedure involves an evaporative emission canister purge, a fuel flush, diurnal heat-build, an LA4 driving cycle, and engine-off and idle periods. For this study, the canister purge was excluded because the effect of the vehicle's canister was eliminated from these tests.
2. All exhaust emission tests were conducted with the vehicle's air intake system connected to the oxygen-enrichment system.
3. The diurnal heat build was not performed because the evaporative emission canister was eliminated from the intake-air system of the engine.
4. A single LA4 preconditioning cycle was run to condition the vehicle before the first set of FTP and off-cycle tests were conducted at specified oxygen concentrations. For subsequent tests at the same oxygen concentration, preconditioning was not carried out, because the effect of the evaporative emission canister was eliminated from this study.
5. The off-cycle emission tests were conducted by using the EPA's REP05 driving schedule, as shown in Figure 2. These tests were conducted immediately after the FTP test, with the first 505 s of the FTP driving cycle used as an engine warm-up procedure. Exhaust emissions were collected for analysis in three bags (Figure 2) as they were in the FTP test, rather than in two bags per the EPA test. The factors used to obtain time-weighted-average emissions were 0.2807, 0.5729, and 0.1464 for bag 1, bag 2, and bag 3, respectively.

The "shake-down" emission tests were conducted using M85 at three intake-air oxygen concentrations. The specific tests were (1) cold phase for 505 s with ambient air, (2) complete FTP, (3) off cycle with 23% oxygen-enriched air, and (4) cold or hot phase for 505 s with 25% oxygen-enriched air. One of the main purposes of these tests was to document the constant oxygen concentrations and low-pressure changes of the intake air when the enhanced air-handling unit was used with this vehicle. M85 was used in these tests to provide samples of

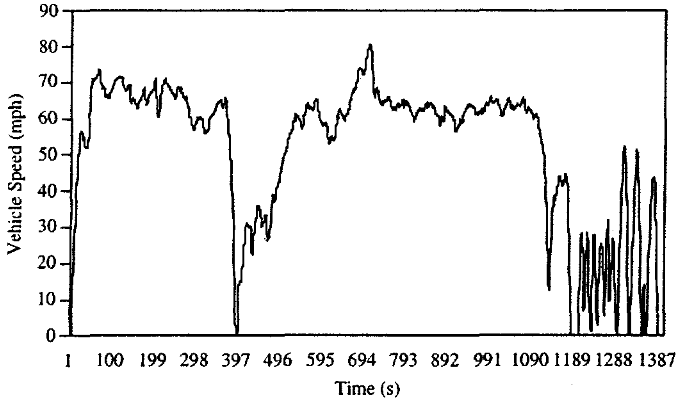

Figure 2. Off-cycle test (EPA-REPOS)

emissions from this specific fuel for speciation. In addition to the FTP and off-cycle tests, an additional FTP was conducted to collect regulated and speciated emission data during only the first 127 s of the cold-phase FTP. Nominal oxygen concentrations of 21%, 23%, and 25% by volume were used for the intake air of the vehicle.

SPECIATION ANALYSES - Complete speciation of HCs, aldehydes, ketones, and alcohols was conducted on the diluted exhaust samples for each of the three phases of the FTP test. A background (dilution air) sample was also speciated for the second phase of the emission test. HC speciation of each sample was conducted by means of gas chromatography to quantitatively identify more than 200 HCs. Aldehyde and ketone speciation was conducted by passing the diluted exhaust samples and a continuous background sample through silica gel cartridges impregnated with 2,4-dinitrophenylhydrazine and then analyzing the aldehyde and ketone derivatives by means of high-performance liquid chromatography. Alcohols were collected using the water-impinger method and analyzed by gas chromotography. Additional details of the speciation procedures used are given in Reference 16. The data were reported in terms of milligrams per mile for each phase of the FTP emissions test for each compound, in addition to the total weighted grams per mile. To obtain speciation samples for the first 127 s of the cold-phase test, a separate set of timers was set up to start and stop the flow of diluted exhaust to a nominal 2-L Tedlar bag and aldehyde/ketone and alcohol carts.

RESULTS AND DISCUSSION

All emission data presented are the averages of two or three separate FTPs and two separate off-cycle emission tests conducted under similar operating conditions and by following similar procedures. The data on THC, NMHC, NMOG, aldehyde, and unburned methanol (CH_3OH) levels in the exhaust were obtained from the HC/aldehyde/alcohol speciation analyses. Data on THC levels obtained directly from the flame ionization detector (FID) instrument were also presented for comparison (represented as THC-FID). From the HC speciation analyses, more than 200 HCs were identified in both engine-out and converter-out exhaust, but only the most significant species were selected (including the four regulated toxics) to report and discuss. To facilitate the discussion, these species are grouped into alcohols, aldehydes, olefins, aromatics, and paraffins. The maximum ozone-forming potential (OFP) and specific reactivities (SRs) were estimated on the basis of maximum incremental reactivity (MIR) and maximum ozone incremental reactivity (MOIR) factors suggested by the California Air Resources Board (CARB) [17]. The percentage reduction or increase in various emissions as a result of using oxygen-enriched intake air (compared with ambient intake air) was calculated as follows:

$$\text{Percent variation} = \frac{\left[\begin{array}{c}\text{mass emissions}\\ \text{with ambient air}\end{array} - \begin{array}{c}\text{mass emissions}\\ \text{with } O_2\text{-enriched air}\end{array}\right] \times 100}{\begin{array}{c}\text{mass emissions}\\ \text{with ambient air}\end{array}} \qquad (1)$$

ENGINE-OUT FTP EMISSIONS - Data on the engine-out exhaust emissions (THC-FID, CO, and NO_x) from the FTP test cycle when nominal 21%, 23%, and 25% oxygen levels were used in the intake air and M85 was the test fuel are presented in Figure 3. Results indicate that THC-FID decreased when the oxygen level was increased from 21% to 23% or 25%. However, CO emissions did not vary appreciably, and NO_x emission levels were higher with 23% or 25% oxygen-enriched air. The reduction in THC-FID was particularly significant during the cold-phase (bag 1) FTP. For example, during the cold-phase FTP, THC-FID emissions decreased from 2.68 g/mi to 1.76 g/mi (34% reduction) and 1.54 g/mi (42% reduction) when 23% and 25% oxygen-enriched intake air was used, respectively, instead of ambient air. The corresponding NO_x emissions increased from 4.4 to 6.5 and 7.9 g/mi, respectively. It is presumed that the availability of higher oxygen concentrations and higher temperatures during combustion result in decreased engine-out THC-FID and increased NO_x emission levels. The availability of oxygen during combustion was greater because of the increase in oxygen concentration in both the oxygen-enriched intake air and the M85 fuel. CO emissions did not change appreciably with the increase in the oxygen level of the intake air, presumably because additional oxygen was also available from the oxygenated M85 fuel. Engine-out NMHC, NMOG, formaldehyde (HCHO), and unburned CH_3OH emission levels (Figure 4) were lowered considerably in the entire FTP cycle when the oxygen content of the intake air was either 23% or 25% instead of 21%. Formaldehyde emissions were reduced by about 53% in bag 1, 84% in bag 2, and 59% in bag 3 of the FTP cycle with 25% oxygen-enriched air. During the cold-phase FTP, reductions of about 60% in NMHCs, 45% in NMOGs, and 40% in unburned methanol were observed when 25% oxygen-enriched intake air was used instead of ambient air.

The demands on conventional three-way catalytic converters during the initial engine start-up and warm-up periods are more severe because of poor converter efficiencies. Engine-out exhaust emission levels are also higher because of the engine's operating characteristics (such as incomplete or partial combustion resulting from rich fuel-to-air mixtures and/or cold engine block and cold exhaust manifold). During these periods, many catalysts tend to partially oxidize unburned methanol to formaldehyde. In some cases, tailpipe formaldehyde emissions might far exceed engine-out formaldehyde emissions because of the increase in partial oxidation of the unburned methanol [5]. However, if the engine produces less unburned methanol, the amount of formaldehyde formed during this period can be

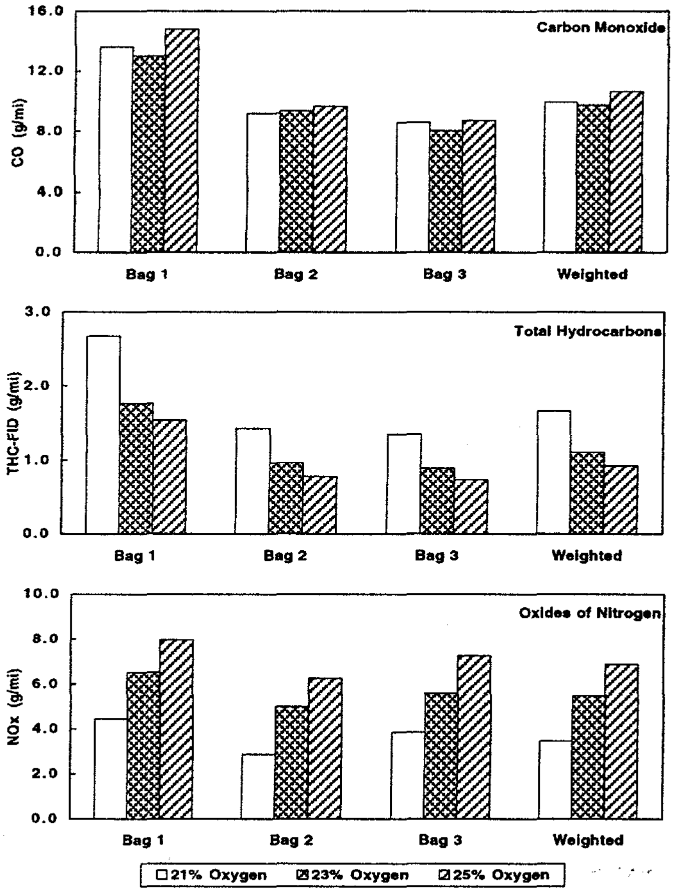

Figure 3. Engine-out THC-FID, CO, and NO_x emissions: FTP cycle with M85

reduced. Another approach for reducing aldehyde emissions, particularly during cold-start and warm-up periods, is to reduce engine-out aldehyde emissions. Ideally, the combination of the faster warm-up characteristics of the converter and the lower level of engine-out unburned methanol and formaldehyde emissions is expected to result in minimum formaldehyde in the converter-out emissions. The presence of enriched oxygen in the combustion air can increase oxidation of methanol and aldehydes formed during the combustion and also can promote complete oxidation of gasoline-derived combustion products. As a result, the engine-out unburned methanol and formaldehyde emissions are considerably reduced when oxygen-enriched intake air is used. The reductions obtained in engine-out unburned methanol and formaldehyde emission levels when 25% oxygen-enriched air is used are evident in Figure 4. These reductions lower the demands on the converter, particularly during the converter warm-up period.

The FTP-cycle, averaged, engine-out HC emission results (from the speciation analyses) with ambient air and 25% oxygen-enriched air are provided in Table 2. Among the aldehydes, formaldehyde and acrolein were significantly reduced, particularly in bag 1 of the FTP cycle (by about 59% and 98%, respectively). However, little variation occurred in acetaldehyde and benzaldehyde when 25% oxygen-enriched intake air was used. During the bag 1 FTP cycle, reductions from 38% to 73% were observed in olefins (ethene, propene, isobutylene, and 1,3-butadiene), aromatics (benzene, toluene, and m-xylene), and paraffins (methane, ethane, n-pentane, n-hexane, and 2,2,4 trimethylpentane) as a result of using the 25% oxygen-enriched intake air. A similar benefit of a reduction in HC emissions was realized in bag 2 and bag 3 when 25% oxygen-enriched intake air was used, but to a lesser extent. Since the bag 1 contribution is very significant when compared with other parts of the FTP cycle, the reductions obtained when 25% oxygen-enriched intake air is used can lead to fewer weighted-average emissions. With oxygen-enriched intake air, the reductions obtained in aldehydes and olefins (reactive species) will lead to a lower level of ozone formation, and the reductions obtained in aromatics and paraffins will help reduce the converter limitations by converting them into more harmless species. Data on the OFP and SR from engine-out exhaust during the FTP cycle, which were calculated on the basis of both MIR and MOIR factors with ambient air and 25% oxygen-enriched intake air, are provided in Table 3.

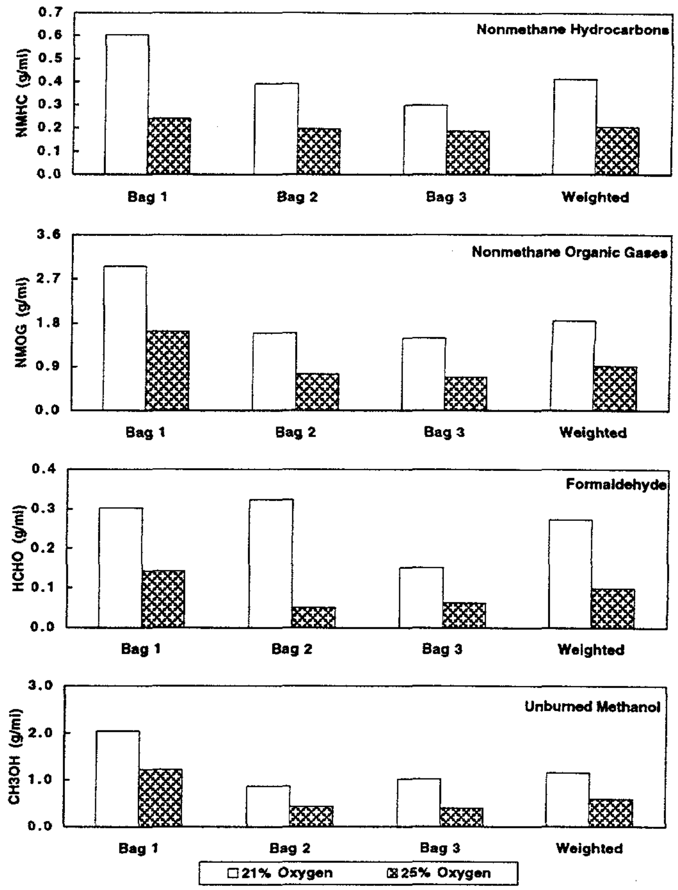

Figure 4. Engine-out NMHC, NMOG, HCHO, and CH_3OH emissions: FTP cycle with M85

The THCs emitted from LDVs are greatest during the cold-phase FTP because of limitations with respect to the heating characteristics of the converter and the engine's operating conditions. Consequently, both OFP and SR are of greater significance during this period. Oxygen enrichment changes the exhaust composition and also reduces the amount of HCs emitted, so that OFP is lowered with oxygen-enriched air. Results indicate that OFP (based on MIR) was reduced by about 45% in bag 1 and about 48% in the weighted average of the FTP cycle when 25% oxygen-enriched intake air was used. The SR variation depends on the maximum OFP estimated and total NMOG. When 25% oxygen-enriched intake air was used, the

Table 2. Averaged engine-out hydrocarbon emissions (mg/mi): FTP cycle with M85

	Bag 1		Bag 2		Bag 3		Weighted	
Hydrocarbon	21% O_2	25% O_2	21% O_2	25% O_2	21% O_2	25% O_2	21% O_2	25% O_2
Alcohols								
Methanol	2049.6	1228.33	864.281	436.4	22.09	402.37	1152.95	591.13
Ethanol	2.39	6.96	1.75	8.71	0.00	17.94	1.4	10.89
Aldehydes								
Formaldehyde	302.74	142.45	323.91	99.70	152.03	63.16	272.34	98.52
Acetaldehyde	3.29	3.61	8.50	3.77	4.01	2.00	6.19	3.25
Acrolein	40.23	0.41	0.42	0.39	0.22	0.19	8.61	0.34
Benzaldehyde	0.00	0.62	0.00	0.58	0.00	0.56	0.00	0.58
Olefins								
Ethene (Ethylene)	94.84	46.12	77.20	42.91	62.88	40.05	76.92	42.79
Propene (Propylene)	57.81	22.71	43.90	18.43	33.95	16.67	44.04	18.84
Propadiene	2.29	1.42	1.28	0.85	1.27	1.23	1.49	1.07
Isobutylene	29.28	11.80	23.90	12.40	16.26	10.32	22.91	11.71
1,3-Butadiene	4.89	2.79	4.49	2.48	3.36	2.56	4.26	2.57
Aromatics								
Benzene	22.87	12.04	11.43	10.88	13.10	9.45	14.26	10.73
Toluene	9.02	5.46	6.21	5.66	6.02	4.18	6.74	5.22
m-Xylene	4.61	1.96	3.77	3.07	2.37	2.00	3.56	2.55
Paraffins								
Methane	102.82	57.17	74.20	41.28	52.77	40.72	74.24	44.42
Ethane	5.64	2.90	5.02	2.40	3.15	2.32	4.64	2.48
n-Pentane	10.78	2.88	6.04	2.57	4.61	2.50	6.63	2.62
n-Hexane	5.93	2.35	3.00	1.35	2.08	1.34	3.36	1.55
2,2,4 Trimethylpentane	28.09	7.69	12.69	4.38	10.01	4.75	15.14	5.16

Table 3. Averaged engine-out ozone-forming potential and specific reactivity: FTP cycle with M85

	Ozone-Forming Potential (g ozone/mi)				Specific Reactivity (g ozone/ g NMOG)			
	MIR		MOIR		MIR		MOIR	
	21% O_2	25% O_2	21% O_2	25% O_2	21% O_2	25% O_2	21% O_2	25% O_2
Bag 1	6.742	3.663	2.835	1.700	2.277	2.257	0.957	1.047
Bag 2	5.132	2.424	2.019	1.091	4.431	3.254	1.743	1.464
Bag 3	2.952	2.020	1.222	0.946	2.001	3.001	0.828	1.406
Weighted	5.021	2.570	2.046	1.177	2.730	2.834	1.113	1.298

SR did not vary appreciably from that of ambient intake air during bag 1 and bag 3 of the FTP cycle. However, the SR did decrease from 4.43 to 3.25 g of ozone per g of NMOG during the bag 2 FTP because of 25% oxygen-enriched intake air.

Cold-phase FTP exhaust emissions were of particular interest in this study. Hence, the time-resolved, engine-out exhaust emissions of THC-FID, CO, and NO_x emissions were analyzed in detail during the first 127-s period; they are shown in Figure 5. The time-resolved emission data exhibited lower THC-FID, higher NO_x, and marginally lower CO emission levels when 25% oxygen-enriched intake air was used instead of ambient intake air. Significant THC-FID emissions during the first 127-s cold-phase FTP are evident in Figure 5, contributing to the much lower THC-FID mass emissions during the FTP bag 1 period. The reduction in THC-FID varied by about 100 to 450 parts per million (ppm) from several cyclic peak values during the first 127-s period when either 23% or 25% oxygen-enriched air was used. The reduction in THC-FID with oxygen enrichment was realized as early as during the first 20-s (key-on and idling) period. CO emission levels were observed to be relatively lower during the idling and first acceleration period of the 127-s period when oxygen-enriched intake air was used instead of ambient intake air. Perhaps the additional oxygen available through intake air helped in complete combustion during the fuel-rich conditions for the first 30 s of vehicle operation. Consequently, CO emission levels were relatively lower during the initial 25 s of the initial cold-start period with 23% or 25% oxygen-enriched air. NO_x emission levels were found to be higher with oxygen-enriched intake air than with ambient intake air. Although NO_x emission levels did not go up during the key-on and idling periods (up to about 20 s), they started increasing from the first acceleration of the vehicle.

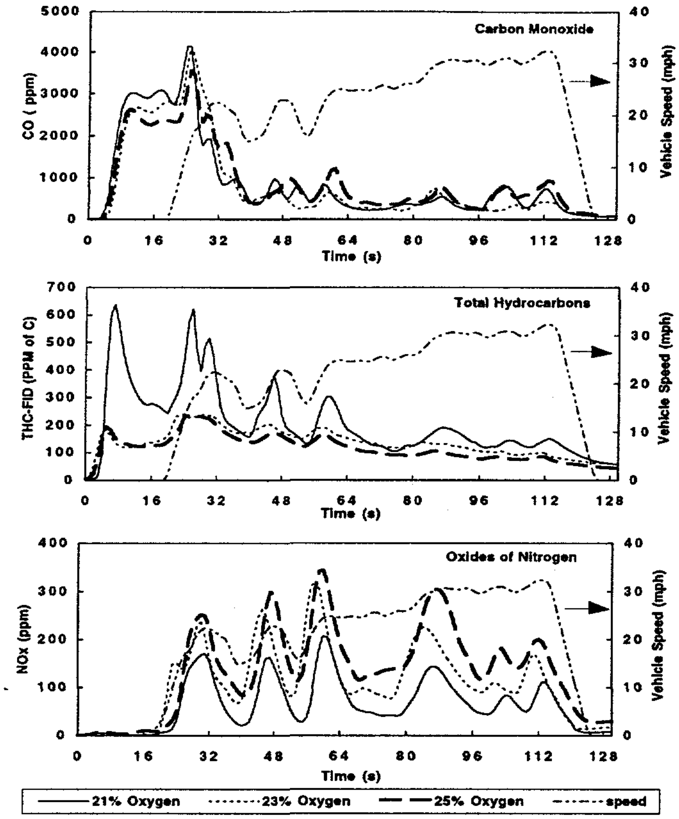

Figure 5. Engine-out emissions during the first 127 s of the cold phase: FTP cycle with M85

Thereafter, NO_x increased with an increase in oxygen enrichment. It was anticipated that higher flame speeds (generally observed with M85), higher combustion temperatures, and additional oxygen availability would lead to an increase in the NO_x level when oxygen-enriched air was used.

CONVERTER-OUT FTP EMISSIONS - The catalytic converter in the test vehicle was unaged (an odometer reading of 3,364 km). It is understood that unaged catalyst systems may not provide a definite indication of long-term performance; however, the present preliminary evaluation allows relative comparisons of emission reductions to be made when different oxygen concentrations are employed in the engine intake air.

The converter-out exhaust emissions obtained with oxygen enrichment are illustrated in Figures 6 and 7. It was observed that THC-FID levels were lower, NO_x levels were higher, and no appreciable variation in CO emissions occurred when 23% or 25% oxygen-enriched intake air was used. Using oxygen-enriched intake air instead of ambient air reduced the THC-FID in bag 1 FTP by about 12-16%. During the bag 2 and bag 3 periods of the FTP cycle, the THC-FID levels from converter-out emissions were also reduced when oxygen-enriched intake air was used, but they were difficult to distinguish quantitatively because the emission levels were very low. Because of lower bag 1 THC-FID emission levels, the FTP-weighted averages of THC-FID emission levels were also lower by about 18% and 21% with 23% and 25% oxygen-enriched intake air, respectively. The effects of oxygen-enriched intake air on THC-FID during the cold-phase FTP are also evident by observing time-resolved and cumulative emission levels shown in Figures 8 and 9, respectively. Evidently, the reductions in engine-out and converter-out THC-FID emissions are more significant during the initial period (up to 300 s) of the cold-phase FTP. The cumulative THC emission data indicate that the engine-out emission levels were much lower when oxygen-enriched intake air was used, particularly with 25% oxygen enrichment. However, unlike engine-out emissions, the reduction in converter-out THC-FID emissions was not pronounced.

The CO emissions were essentially similar with ambient air and oxygen-enriched air. This result was anticipated because of the increase in oxygen content from both the fuel and the intake air during combustion. As was the case for engine-out emissions, the NO_x emission levels were much higher with oxygen enrichment. The weighted-average NO_x emissions increased from 0.083 g/mi with ambient air to 0.307 and 0.51 g/mi with 23% and 25% oxygen-enriched air, respectively. The NMHC emissions were reduced by about 38% in bag 1, 66% in bag 2, and 52% in bag 3 with 23% oxygen-enriched air, and they were reduced by about 89% in bag 1, 66% in bag 2, and 72% in bag 3 with 25% oxygen-enriched air. The converter-out emission levels of NMOG, formaldehyde, and unburned methanol were little affected by the use of oxygen-enriched intake air, contrary to the observed greater reductions in engine-out emissions. This minimal effect could possibly be a result of the variation of catalytic reactions in the converter due to changes in the engine-out exhaust composition.

Studies at Ford [5] and elsewhere [18] have shown that catalytic alcohol oxidation always shows some evidence for a series mechanism, i.e.,

$$\text{Alcohol} \longrightarrow \text{Aldehyde} \xrightarrow{O_2} CO_2 + H_2O \qquad (2)$$

The above series reaction 2 suggests that aldehyde yield should be minimal when there is a large excess of O_2 available to drive the reaction completely to CO_2 and H_2O yet not enough O_2 to oxidize the catalyst [5]. When oxygen-enriched intake air was used, the exhaust oxygen contents were relatively higher, particularly during the initial start-up and warm-up periods, than when ambient intake air was used. Accordingly, in the presence of a catalyzing environment, the additional oxygen available in the exhaust could participate in the oxidation of aldehyde [see EQ. (2)] and also in the oxidation of unburned methanol and reactive olefins and paraffins. Another important aspect of the catalytic reactions in the converter is the presence of NO_x. The fraction of NO_2 in NO_x is considerably higher in methanol combustion products because of the conversion of NO to NO_2, which occurs when formaldehyde is formed from methanol [19,20]. Methanol oxidation, and the chemical reactions involving NO_2 in the catalyst, are represented by:

$$CH_3OH + OH \text{------>} CH_2OH + H_2O \qquad (3)$$

$$CH_2OH + O_2 \text{------->} CH_2O + HO_2 \qquad (4)$$

$$NO + HO_2 \text{------->} NO_2 + OH \qquad (5)$$

$$CH_3OH + NO_2 \text{------>} CH_2OH + HNO_2 \qquad (6)$$

$$HNO_2 \text{-------->} NO + OH \qquad (7)$$

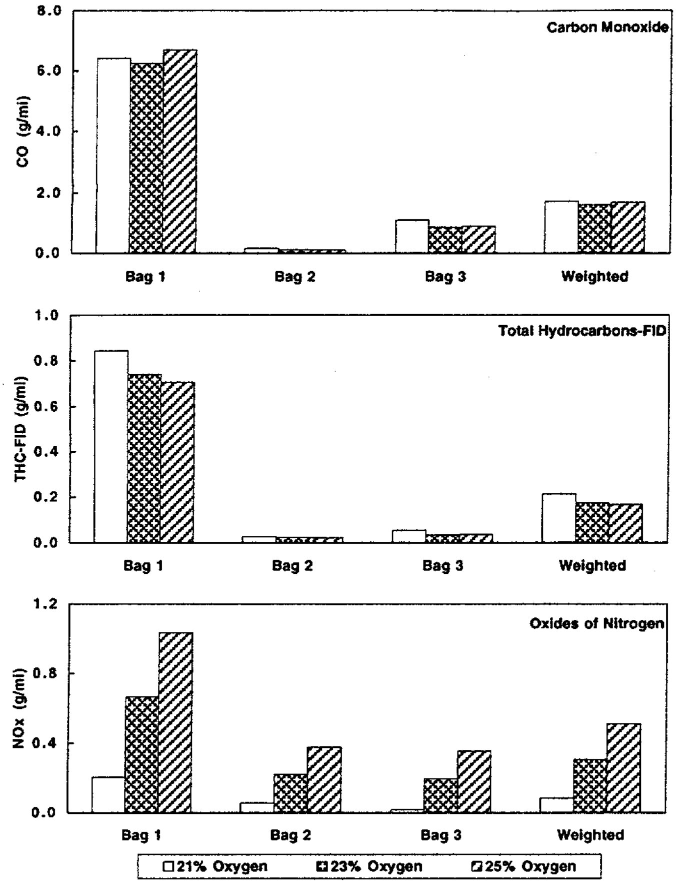

Figure 6. Converter-out THC-FID, CO, and NO_x emissions: FTP cycle with M85

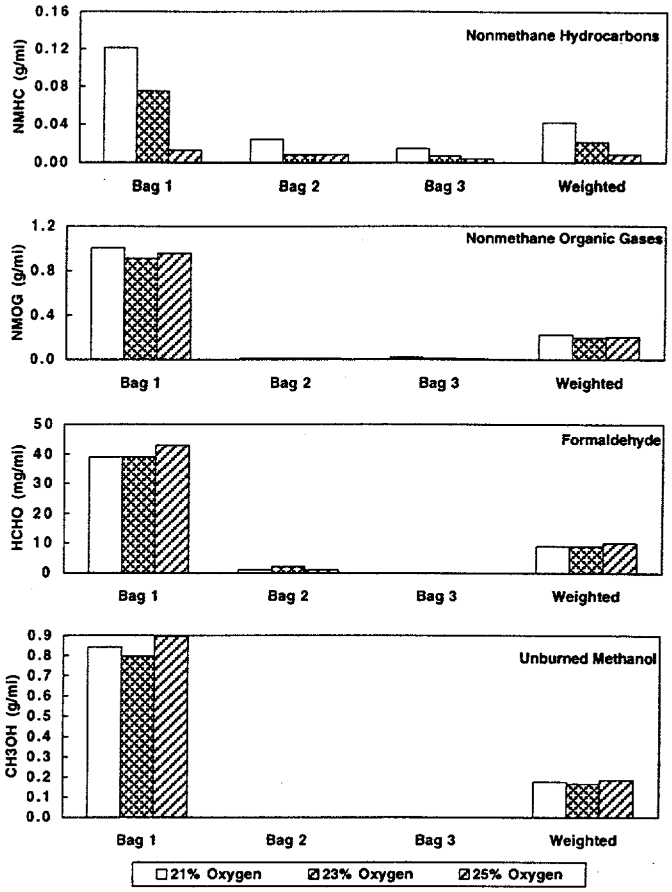

Figure 7. Converter-out NMHC, NMOG, HCHO, and CH_3OH emissions: FTP cycle with M85

Reaction 4 is a major step when formaldehyde forms from methanol, and it produces a large amount of HO_2. NO_2 is mainly formed by Reaction 5 and acts to initiate the chain reaction for alcohol oxidation by Reaction 6. NO_2 is more effective than NO as an oxidizer [19]. Methanol promotes the reduction of NO_2 to NO from Reactions 6 and 7. NO_2 reduction, accompanied by methanol oxidation in an oxidation catalyst, occurs even in excess oxygen. The supply of O_2 atoms for the unburned species at the catalyst surface results from competition between NO_2 and O_2 as an oxidizer. Consequently, it is expected that the large amount of NO_2 in NO_x will affect the oxidation of unburned methanol and formaldehyde in an oxidation catalyst. When oxygen-enriched intake air was used, the engine-out exhaust consisted of relatively higher NO_x and O_2 levels but relatively lower unburned methanol and formaldehyde emission levels. In light of the above complex chemical reactions involving NO_x and O_2 in the methanol and formaldehyde oxidation processes, the net formaldehyde tailpipe emissions are difficult to estimate, and more difficult to predict when a deactivated catalyst is used. The composition of the engine-out exhaust when oxygen-enriched intake air was used was quite different from that obtained when ambient intake air was used. Hence, detailed laboratory experiments and vehicle studies that use oxygen-enriched intake air would be necessary to elucidate the methanol and formaldehyde oxidation processes in the converter and also to evaluate an optimum level of oxygen enrichment to yield the lowest possible formaldehyde emission level.

Earlier studies [2] clearly pointed out that the formaldehyde emissions sharply increase as mileage accumulates. The worst-case tailpipe formaldehyde emissions will increase, at most, to engine-out levels as the catalyst deactivates. As a catalyst ages, the peak amount of formaldehyde increases and, in addition, the temperature of maximum formaldehyde production and the light-off temperature [5] shift to higher temperatures. The catalyst deterioration from using oxygen-enriched intake air can be tolerated to a certain extent because it results in lower engine-out unburned methanol and formaldehyde emission levels. This effect can be noticed from the converter efficiency tolerance (difference in conversion efficiencies between ambient intake air and oxygen-enriched intake air) obtained for THC-FID emission conversions with oxygen-enriched intake air during the cold-phase FTP, as shown in Figure 10. As long as the catalyst's deactivation as mileage accumulates falls within the above converter efficiency tolerance range, the vehicle is expected to produce the THC-FID levels of an unaged catalyst. Figure 10 shows that 23% or 25% oxygen-enriched intake air results in a considerable converter efficiency tolerance, particularly during the initial 200 s of the cold-phase (about 10%-40%). This feature could possibly alleviate the converter performance limitations during the cold-phase FTP as mileage accumulates. To verify such an application, more experiments need to be conducted with a sufficiently aged catalyst.

From the HC/aldehyde/methanol speciation of converter-out exhaust during the FTP cycle, the variations in

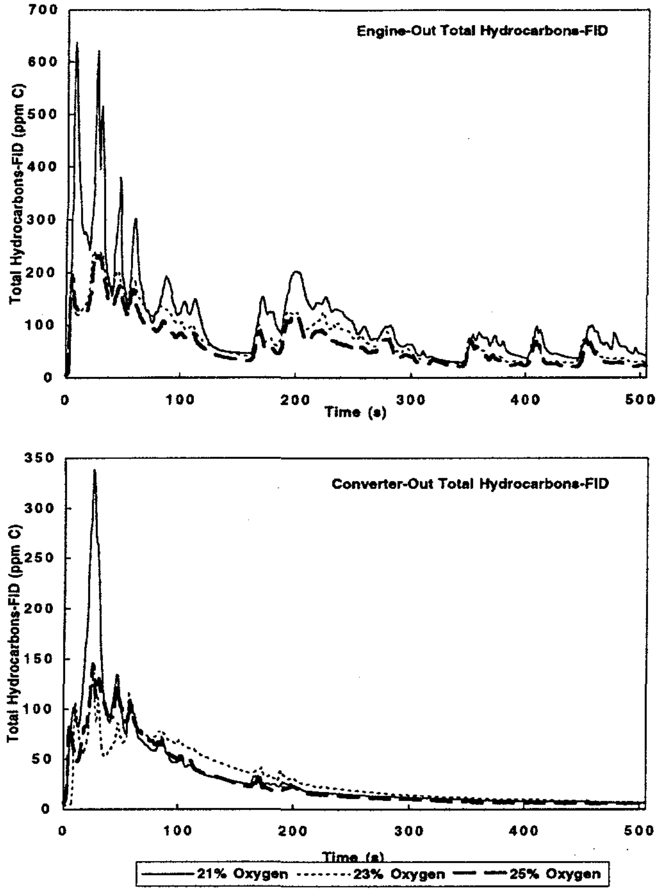

Figure 8. Engine-out and converter-out total hydrocarbon emissions during cold-phase FTP

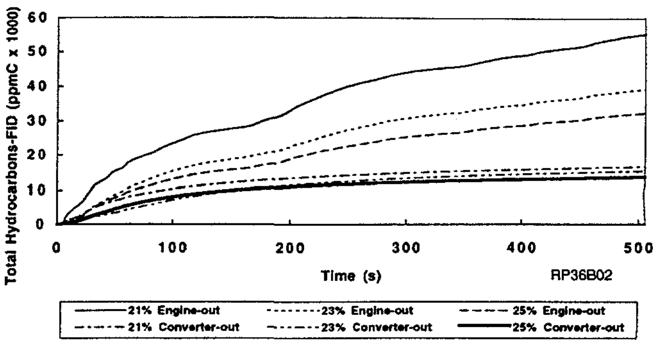

Figure 9. Cumulative engine-out and converter-out average THC-FID emissions during cold-phase FTP

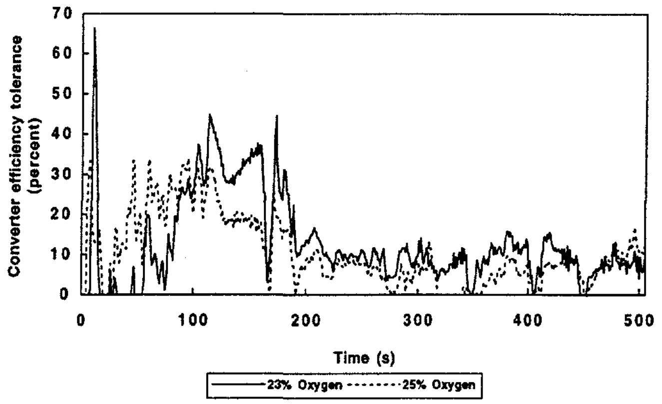

Figure 10. Converter efficiency tolerance with oxygen-enriched intake air during the cold-phase FTP

some of the emissions of aldehydes, olefins, aromatics, and paraffins with oxygen-enriched intake air are presented in Table 4. The FTP weighted-average formaldehyde emission levels were lower than 10 mg/mi for both ambient air and oxygen-enriched intake air. In general, converter-out aldehyde emissions were not greatly affected by oxygen-enriched intake air, unlike the case for engine-out aldehyde emissions. This result occurred partly because of the very low levels of acetaldehyde, acrolein, and benzaldehyde in the converter-out emissions, even when ambient air was used. The lowest level of aldehydes achieved in a given converter might also be limited because several oxidation and reduction reactions take place simultaneously as functions of the engine-out exhaust composition and temperature. Studies with sufficiently aged catalysts or converters with poor conversion efficiencies might reveal the potential advantages of oxygen-enriched intake air in reducing aldehyde emissions. Among the olefins, ethene and propene were reduced by about 21-62% with oxygen-enriched intake air, the highest reductions being achieved with 25% enrichment. From the aromatics group, benzene (which is a regulated toxic) and toluene were reduced by about 53% and 67%, respectively, from the use of either 23% or 25% oxygen-enriched intake air. However, there was little variation in m-xylene. With 23% or 25% oxygen-enriched intake air, most of the paraffins (methane, ethane, n-pentane, and n-hexane) were reduced by about 27-67%. It appears that oxygen-enriched intake air helps oxidize the majority of aromatics and helps oxidize paraffins (which are generally difficult to oxidize) in the converter. Reactive species, such as ethene and propene, which are believed to contribute significantly to ozone formation and photochemical smog, were also considerably reduced when oxygen-enriched intake air was used. These reductions could possibly result from lower engine-out HC emission levels and also from the relatively higher oxygen content in the exhaust gases.

Of the more than 200 HC compounds identified quantitatively from the HC speciation analysis, about 40 are considered major contributors (high OFP) to ozone formation. The list of these compounds is given in the appendix. When either 23% or 25% oxygen-enriched intake air was employed, the OFPs of all 40 were considerably reduced because of lower HC emissions. Data on reductions obtained in OFP (on the basis of MIR and MOIR factors) for both engine-out and converter-out emissions from using 23% and 25% oxygen-enriched air during the cold-phase FTP are provided in the appendix. The averaged converter-out OFP and SR on the basis of MIR and MOIR factors are provided in Table 5. Because of reductions in the OFP of various HC components due to oxygen-enriched intake air, the maximum OFP was also lowered. However, unlike the greater reductions in engine-out OFP, converter-out OFP reductions of about 10% and 30% were observed with 23% and 25% oxygen-enriched intake air, respectively. OFP levels can also be considered when one evaluates the failure of the LEV and ULEV classes to reach the lower limit for NMOG when M85 is used. For LEV and ULEV, the OFP must be less than 0.25 g of ozone per mile and 0.125 g of ozone per mile,

Table 4. Averaged converter-out hydrocarbon emissions (mg/mi): FTP cycle with M85

	Bag 1			Bag 2			Bag 3			Weighted		
Hydrocarbon	21% O_2	23% O_2	25% O_2	21% O_2	23% O_2	25% O_2	21% O_2	23% O_2	25% O_2	21% O_2	23% O_2	25% O_2
Alcohols												
Methanol	869.27	795.59	831.81	5.14	0.00	0.00	1.57	0.00	0.00	183.36	164.65	172.38
Ethanol	1.64	0.00	1.08	0.88	0.55	0.00	2.62	0.00	0.00	1.52	0.28	0.23
Aldehydes												
Formaldehyde	33.46	38.86	33.46	0.60	2.28	1.29	0.43	0.47	0.44	8.24	9.35	7.72
Acetaldehyde	0.74	0.73	0.74	0.40	0.06	0.16	0.49	0.00	0.13	0.58	0.18	0.27
Acrolein	0.16	0.18	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.04	0.03
Benzaldehyde	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Olefins												
Ethene (Ethylene)	9.45	7.46	4.58	0.00	0.00	0.00	0.00	0.00	0.00	1.96	1.54	0.95
Propene (Propylene)	3.13	2.16	1.18	0.00	0.00	0.00	0.00	0.00	0.00	0.65	0.45	0.25
Propadiene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isobutylene	2.27	1.68	2.92	0.00	0.45	1.13	0.00	1.56	1.30	0.00	1.01	1.55
1,3-Butadiene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatics												
Benzene	5.72	2.40	1.87	0.79	0.00	0.00	0.80	0.00	0.40	1.82	0.50	0.50
Toluene	3.24	1.09	1.53	0.94	0.13	1.69	0.63	0.11	0.45	1.33	0.32	1.32
m-Xylene	0.53	1.07	0.81	0.00	0.27	0.00	0.00	0.18	0.33	0.11	0.41	0.26
Paraffins												
Methane	40.30	28.53	22.26	7.84	2.47	3.34	12.63	10.08	7.76	15.89	9.95	8.48
Ethane	1.25	0.62	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.13	0.10
n-Pentane	3.58	1.63	1.16	0.92	0.40	0.55	0.64	0.11	0.54	1.39	0.58	0.67
n-Hexane	2.47	1.81	0.67	0.22	0.17	0.13	0.26	0.13	0.10	0.70	0.50	0.23
2,2,4 Trimethylpentane	2.47	5.63	2.38	0.58	0.00	0.19	0.96	0.37	0.15	2.48	1.27	0.63

Table 5. Averaged converter-out ozone-forming potential and specific reactivity: FTP cycle with M85

	Ozone-Forming Potential (mg ozone/mi)						Specific Reactivity (g ozone/g NMOG)					
	MIR			MOIR			MIR			MOIR		
	21% O_2	23% O_2	2% O_2	21% O_2	23% O_2	25% O_2	21% O_2	23% O_2	25% O_2	21% O_2	23% O_2	25% O_2
Bag 1	1424.300	1278.984	1181.326	707.950	635.494	598.017	1.419	1.405	1.285	0.705	0.698	0.651
Bag 2	77.416	54.094	58.458	35.004	21.711	23.207	3.139	5.409	4.497	1.419	2.171	1.785
Bag 3	108.648	75.439	83.453	61.359	46.048	45.212	6.268	10.777	10.432	3.540	6.578	5.652
Weighted	365.310	313.471	298.109	181.811	155.429	148.407	1.619	1.599	1.491	0.806	0.793	0.742

respectively [21]. When 25% oxygen-enriched intake air was used, the maximum OFP obtained was close to the LEV limit (0.298 g/mi). It appears that oxygen-enriched intake air and a method to increase the warm-up rate of the converter during the initial start-up period have the potential to meet LEV/ULEV standards.

The SR was relatively lower during bag 1 FTP (reduced from 1.419 to 1.285 g of ozone per g of NMOG) when 25% oxygen-enriched intake air was used. As a result, the weighted average SR was also reduced from 1.619 to 1.49 gram ozone per gram NMOG. However, the SR was relatively higher during bag 2 and bag 3. These findings indicate that greater reductions in both SR and NMOG were difficult to obtain from using oxygen-enriched intake air. This result evidently occurs because reductions are greater for NMOG than for OFP. For vehicles to meet LEV/ULEV standards, lower levels of both SR and NMOG are desirable. These effects warrant conducting further investigations on using oxygen-enriched intake air to optimize oxygen-fuel ratios and other operating conditions during the cold phase, a method that could lead to lower SR as well as NMOG levels.

In general, vehicles running on alternative fuels have a considerably smaller OFP despite nominally equal NMOG emissions because of the lower reactivity of the emission components. The CARB methods take the different reactivities of the emissions within the NMOG limits of the emission classes into consideration. They do so by introducing reactivity adjustment factors (RAFs) that are to be defined for all relevant alternative fuels in the three LEV emission classes. The RAF is defined as the quotient of the specific reactivity of the alternative fuel (clean fuel) and the specific reactivity of the "reference fuel" for emissions and certificate tests [21,22]:

$$RAF = \frac{SR_{Clean\ Fuel}}{SR_{Reference\ Fuel}} \qquad (8)$$

The measured NMOG value of a vehicle is multiplied by the corresponding RAF; the result is then compared with the legally specified NMOG limit. Manufacturers have two options when using a RAF for a given fuel. They can establish their own SR for a particular engine family (to be used in the numerator of the RAF equation), or they can use the generic RAF developed by CARB, which applies to all vehicles and fuels in a given emission category (TLEV, LEV, or ULEV). Both options use the same baseline SR (the denominator of the RAF equation) determined by the CARB. The baseline SR and generic RAFs for different alternative fuels, vehicle classes, and emission classes suggested by CARB are provided in Table 6 [22].

In the present work, four different methods were used to obtain reactivity-adjusted NMOG values; they are shown in Table 7 with corresponding RAFs. Reactivity-adjusted NMOG values were calculated on the basis of a generic RAF of 0.41 and on the basis of SRs provided for LEV and ULEV emission classes with M85. Since the reference fuel used by CARB would be different from the reference fuel (Indolene) in the present experiments, the SR based on the Indolene fuel for this particular FFV was also employed to estimate the RAF. After the RAF (with ambient intake air) was obtained, the same procedure was used to compute reactivity-adjusted NMOG values with oxygen-enriched intake air. The computed values based on the four different RAFs are provided in Table 7. Results indicate that with a generic RAF of 0.41, the reactivity-adjusted NMOG was lower than TLEV standards (without considering catalyst deterioration factors) and also very close to meeting the LEV standards when either 23% or 25% oxygen-enriched air was used. The reactivity-adjusted NMOG values calculated by the other methods of computing RAFs were also close to the LEV standards. These lower reactivity-adjusted NMOG values indicate that oxygen-enriched intake air could be a candidate for meeting the future NMOG emission standards.

The converter-out, time-resolved emissions of THC-FID, CO, and NO_x during the first 127-s cold-phase FTP are illustrated in Figure 11. Of these exhaust emissions, THC-FID emissions benefit most from oxygen-enriched combustion. During the initial idling and first transient period of vehicle operation (initial 40 s from key-on), THC-FID emissions were considerably reduced when either 23% or 25% oxygen-enriched air was used. For example, the peak of THC-FID was reduced from about 340 to 140 ppm during the first 30-s period because of 23% or 25% oxygen enrichment. However, there was no appreciable variation in CO emissions because of oxygen-enriched air and M85. The NO_x emission levels were relatively higher when oxygen-enriched air was used. During the initial 127 s of the cold phase, the increase in NO_x with oxygen enrichment was quite noticeable only between the 25-s to 75-s period. The maximum value of NO_x increased from about 80 to 200 ppm with 25% oxygen-enriched air. Because the increase in NO_x was predominant for only about 50 s during the 127-s period of the cold phase, its relative contribution to overall converter-out NO_x emissions would not be severely affected if this technique were to be employed only during the cold-phase FTP or initial 127 s of the cold-phase FTP. Recalibration of the engine control unit (ECU) and optimized spark timing might help alleviate the NO_x problems to a certain extent when oxygen-enriched intake air is used.

The time-resolved emissions data show that the initial 127-s period of the cold phase is crucial for catalytic converters because of catalyst light-off time limitations. If oxygen-enriched intake air was used during only the initial start-up and warm-up periods, the advantages of lower THC and CO emission levels

Table 6. CARB reactivity adjustment factors and baseline specific reactivities for different emission and clean fuel categories

Fuel	Light-Duty Vehicles			Medium-Duty Vehicles	
	TLEV	LEV	ULEV	LEV	ULEV
	Baseline Specific Reactivity (g ozone/g NMOG)				
Conventional gasoline	3.42	3.13	3.13	3.13	3.13
	Reactivity Adjustment Factors				
Phase 2 RFG	0.98	0.94	0.94	0.94	0.94
M85	0.41	0.41	0.41	0.41	0.41
Natural gas	1.00	0.43	0.43	0.43	0.43
LPG	1.00	0.50	0.50	0.50	0.50

Source: Reference 22

Table 7. Reactivity adjusted NMOG (g/mi) : FTP cycle weighted-average with M85

Parameter	Reactivity Adjustment Factor			Reactivity Adjusted NMOG (g/mi)			California Standards (g/mi)	
	21% O_2	23% O_2	25% O_2	21% O_2	23% O_2	25% O_2	TLEV	LEV
CARB-specified RAF (0.41)	0.410	0.410	0.410	0.093	0.080	0.082	0.125	0.075
Specific reactivity (TLEV) = 3.42	0.473	0.468	0.436	0.107	0.092	0.087	0.125	0.075
Specific reactivity (LEV) = 3.13	0.517	0.511	0.476	0.117	0.100	0.095	0.125	0.075
Specific reactivity (Indolene) = 3.74	0.433	0.428	0.399	0.098	0.084	0.080	0.125	0.075

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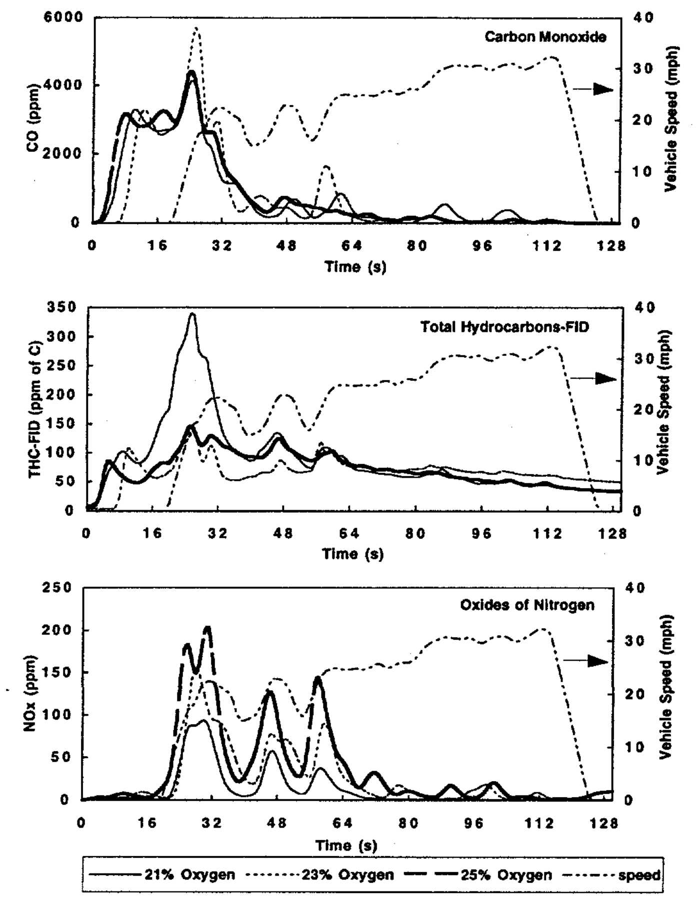

Figure 11. Converter-out emissions during the first 127 s of the cold-phase: FTP cycle with M85

could be obtained while the NO_x emission level could be kept sufficiently low. To investigate application of oxygen-enriched intake air to reduce cold-phase FTP emissions, special tests were conducted in three different ways, as listed below:

1. The 25% oxygen-enriched intake air is supplied only during the initial 127 s of the cold-phase FTP cycle. The remaining 378 s of bag 1, bag 2, and bag 3 of the FTP cycle is supplied with ambient air.
2. The 23% oxygen-enriched air is used only during the cold-phase FTP cycle. In this approach, 23% oxygen-enriched intake air is supplied only during bag 1 of the FTP cycle. During bag 2 and bag 3 periods, ambient air is employed.
3. The 25% oxygen-enriched air is used only during the cold-phase FTP cycle. In this approach, 25% oxygen-enriched intake air is supplied only during bag 1 of the FTP cycle. During bag 2 and bag 3 periods, ambient air is employed.

The results obtained from the above FTP tests, compared with emission standards for LDVs for the year 2004 (Tier II) and with California standards, are shown in Table 8. In the present experiments, the vehicle was driven only about 3,364 km. In the absence of catalyst deterioration factors, it is difficult to assess the benefits of oxygen enrichment after a vehicle has operated 80,467 or 160,934 km (50,000 or 100,000 miles). However, it is expected that engine operation with oxygen-enriched air (23% or 25%) would have similar emission benefits irrespective of vehicle mileage, since such air basically reduces the engine-out emissions. The only exception to this assumption is that a deactivated catalyst produces relatively higher formaldehyde emission levels as mileage accumulates. Test results indicate that when 25% oxygen-enriched air was used during only the first hill (127 s) of the cold-phase FTP cycle, the converter-out weighted-average emissions of formaldehyde, reactivity adjusted-NMOG, CO, and NO_x were all lower than the TLEV and LEV (except NMOG) standards. The increase in NO_x emissions with oxygen-enriched intake air was lower than the standards because the enriched air's relative contributions were modest during the 127-s period of the cycle. When 23% or 25% oxygen-enriched intake air was employed during only the cold-phase FTP, the emission levels were much lower than the TLEV standards and had good potential for meeting LEV/ULEV standards. The results also show that the Tier II standards of NMHC, CO, and NO_x can be met when oxygen-enriched intake air containing 23% or 25% oxygen is used during only the cold-phase FTP. The marginal increase in the NO_x emissions when 25% oxygen-enriched air is used during only cold-phase application can be reduced to a certain extent by proper control of spark timing and recalibration of the ECU to account for increased oxygen concentration. A post-treatment NO_x control

Table 8. Potential of oxygen-enriched intake air to meet future emission standards

	FTP Weighted-Average Emissions (g/mi)				
Case or Standard	Reactivity-adjusted NMOG	Formaldehyde	NMHC	CO	NOx
Case					
(1) Ambient (21% O_2)	0.09499	0.00909	0.0439	1.775	0.0886
(2) 25% O_2 (initial 127 s of bag 1)	0.09605	0.00818	-	2.099	0.1249
(3) 23% O_2 (bag 1 only)	0.08729	0.00917	0.03395	1.725	0.1868
(4) 25% O_2 (bag 1 only)	0.08227	0.00874	0.02062	1.744	0.2153
Emission standards at 50,000 miles					
Tier II (2004)			0.125	1.7	0.2
TLEV	0.125	0.015		3.4	0.4
LEV	0.075	0.015		3.4	0.2
ULEV	0.040	0.008		1.7	0.2

device such as a lean NO_x catalyst or monatomic nitrogen induced by a pulsed arc [12] might also be helpful to comply with the ULEV/Tier II emission standards. The suitability of a given oxygen-enrichment level for a particular vehicle depends on the desired reductions of both THC and CO as well as the simultaneous control of NO_x emissions (without exceeding the emissions standards). For FFVs operating on M85, the combination of an optimum oxygen-enrichment level and reoptimized spark-timing may have the potential to meet Tier II and California standards.

OFF-CYCLE CONVERTER-OUT EMISSIONS - The off-cycle test was developed as one of the driving schedules to represent in-use driving that is outside the boundary of the current FTP driving cycle. The cycle was generated from a composite data set that equally represented Los Angeles chase car data and Baltimore three-parameter instrumented vehicle data. The primary purpose of the cycle is to assess in-use emissions. Figure 12 shows the off-cycle converter-out exhaust emissions of THC-FID, CO, and NO_x with ambient air and two different levels of oxygen enrichment. The emission levels from bag 3 of the off cycle were disproportionately higher than those from other bags because of the rapid accelerations and decelerations involved in the driving cycle. Conventional catalytic converters cannot control these emissions because of the increase in fuel enrichment during periods of rapid accelerations. Under these conditions, oxygen enrichment might play a major role in bringing the air-to-fuel ratio close to stoichiometric and promoting complete combustion. As a result, converter-out THC-FID and CO emissions from bag 3 were considerably reduced. THC-FID was reduced from 0.308 g/mi to 0.149 g/mi (51%) and 0.194 g/mi (37%) with 23% and 25% oxygen-enriched air, respectively. Similarly, CO emissions were reduced from 16.2 g/mi to 5.4 g/mi (66%) and 3.8 g/mi (76%) when the intake oxygen level was increased from 21% to 23% and 25%, respectively. However, the corresponding NO_x emissions increased from 0.21 g/mi to 0.82 g/mi (2.8 times) and 1.7 g/mi (7 times). Although the NO_x emissions from bag 3 were higher with oxygen-enriched air, as a result of relatively low contributions from the other two bags, the weighted-average emissions increased from 0.05 g/mi with ambient air to 0.19 g/mi and 0.49 g/mi with 23% and 25% oxygen-enriched air, respectively. It seems that if oxygen enrichment is employed during only bag 3 of the off-cycle, NO_x emissions can be decreased to a greater extent while the maximum benefits from reducing THC-FID and CO emissions simultaneously are obtained. ECU recalibration to account for higher intake-air oxygen levels and a post-treatment NO_x control device would help decrease the NO_x to very low levels.

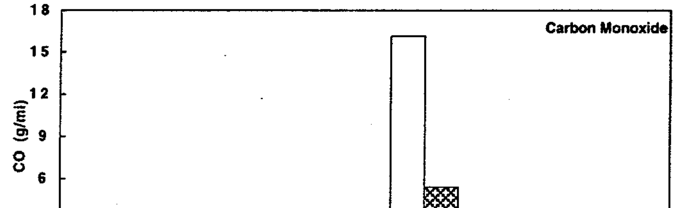

Figure 12. Converter-out exhaust emissions: Off-cycle with M85

CONCLUSIONS

On the basis of present investigations on a 1993 flexible-fuel Dodge Spirit (passenger LDV) with a 2.5-L port-fuel-injected engine and an odometer reading of 3,364 km that uses oxygen-enriched intake air and runs on M85 fuel, the following conclusions are drawn.

1. Oxygen-enriched intake air has the potential to reduce engine-out THCs, unburned methanol, and formaldehyde from FFVs operating on M85, particularly during the cold-phase FTP cycle. However, it has little effect on CO emissions, and NO_x emission levels are higher because of the availability of oxygen in both the intake air and oxygenated fuel.
2. During the cold-phase FTP, reductions of about 42% in THCs, 60% in NMHCs, 45% in NMOGs, and 40% in unburned methanol were observed in the engine-out emissions when 25% oxygen-enriched intake air was used. However, the corresponding NO_x emissions were increased by about 78%. Engine-out formaldehyde emissions, which are of particular concern with regard to FFVs operating on M85, were reduced by about 53% in bag 1, 84% in bag 2, and 59% in bag 3 by following the FTP cycle with 25% oxygen-enriched intake air.
3. Converter-out THC emissions were reduced by about 32% and 64% and NMHC emissions were reduced by about 38% and 89% during the cold-phase FTP from using nominal 23% and 25% oxygen-enriched intake air, respectively. The FTP converter-out, weighted-averages of formaldehyde emissions with 23% or 25% oxygen-enriched intake air were lower than 10 mg/mi. In general, the converter-out NMOG and unburned methanol emissions resulting from using oxygen-enriched air were also lower, but to a lesser extent.
4. The OFP (on the basis of MIR factors) of the FTP converter-out, exhaust HCs was reduced by about 10% to 30% with 23% and 25% oxygen-enriched intake air, respectively. However, the variation in SR with oxygen-enriched intake air was very small. The reactivity-adjusted NMOG level

based on the CARB generic RAF (0.41 for M85) was lower than the California TLEV standards with either 23% or 25% oxygen-enriched intake air.

5. With nominal 23% oxygen-enriched intake air, reductions of about 67% in CO and 52% in THC-FID emissions were observed from the bag 3, converter-out, off-cycle test. However, the corresponding NO_x emission levels were higher (increased from 0.214 to 0.815 g/mi). The increase in NO_x emissions with oxygen-enriched intake air might necessitate a post-treatment control device.
6. The FFVs operating on M85 that used 25% oxygen-enriched intake air during only the initial 127 s of the cold-phase or used 23% or 25% oxygen-enriched intake air during only the cold-phase FTP could meet (without adjusting for catalyst deterioration factors) reactivity-adjusted NMOG, CO, NO_x, and formaldehyde emission standards of the TLEV. An optimized oxygen-enrichment level, coupled with a device to reduce NO_x (for example, using monatomic nitrogen induced by a pulsed arc), has the potential of becoming a viable technology for controlling exhaust emissions from FFVs.

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DISCLAIMER

Appendix

Engine-out and converter-out ozone-forming potential compounds from speciated hydrocarbons during the cold-phase FTP with M85

	mg of ozone/mile (based on MIR)					mg of ozone/mile (based on MOIR)				
	Engine-out		Converter-out			Engine-out		Converter-out		
Compound	21% O_2	25% O_2	21% O_2	23% O_2	25% O_2	21% O_2	25% O_2	21% O_2	23% O_2	25% O_2
Ethene (Ethylene)	691.38	336.21	68.87	54.38	33.39	299.69	145.74	29.85	23.57	14.47
Acetylene (Ethyne)	28.09	20.16	3.91	2.40	0.99	18.54	13.31	2.58	1.58	0.65
Propene (Propylene)	543.41	213.47	29.45	20.30	11.05	217.94	85.62	11.81	8.14	4.43
Benzene	9.61	5.06	2.40	1.01	0.78	3.20	1.69	0.80	0.34	0.26
Toluene	24.62	14.91	8.85	2.98	4.16	5.68	3.44	2.04	0.69	0.96
Methanol	1147.78	687.86	486.79	445.53	465.81	573.89	343.93	243.40	222.77	232.91
Methylacetylene (Propyne)	10.74	2.34	0.00	0.00	0.00	5.69	1.24	0.00	0.00	0.00
Isobutylene	155.48	62.66	12.05	8.92	15.51	56.51	22.77	4.38	3.24	5.64
1,3-Butadiene	53.25	30.38	0.00	0.00	0.00	20.34	11.61	0.00	0.00	0.00
trans-Butene-2	26.24	10.04	0.00	0.00	0.00	9.93	3.80	0.00	0.00	0.00
cis-Butene-2	21.77	7.65	0.00	0.00	0.00	8.23	2.90	0.00	0.00	0.00
3-Methylbutene-1	9.08	4.35	0.00	0.00	0.00	3.59	1.72	0.00	0.00	0.00
Isopentane	291.02	75.59	60.40	29.83	21.87	109.13	28.35	22.65	11.19	8.20
2-Methylbutene-1	9.75	3.23	2.45	1.81	0.93	3.78	1.25	0.95	0.70	0.36
n-Pentane	11.21	3.00	3.72	1.70	1.20	7.33	1.96	2.43	1.11	0.79
2-Methyl-1,3-Butadiene	8.72	2.09	0.00	0.00	0.00	3.27	0.78	0.00	0.00	0.00
trans-Pentene-2	16.10	10.47	2.05	3.52	2.16	6.04	3.93	0.77	1.32	0.81
2-Methylbutene-2	14.55	4.68	4.08	2.50	1.28	5.22	1.68	1.46	0.90	0.46
Cyclopentene	9.96	5.13	0.69	3.29	0.54	3.61	1.86	0.25	1.20	0.19
2-Methylpentane	35.13	11.69	12.87	8.28	3.43	20.66	6.88	7.57	4.87	2.02
3-Methylpentane	21.72	10.00	7.67	6.29	1.83	13.43	6.19	4.74	3.89	1.13
trans-3-Methylpentene-2	51.01	19.20	11.33	11.81	4.68	19.06	7.18	4.23	4.41	1.75
Methylcyclopentane	21.50	8.09	4.78	4.98	1.97	11.82	4.45	2.62	2.74	1.09
2,3-Dimethylbutene-2	14.28	4.85	5.23	3.24	1.29	5.34	1.81	1.95	1.21	0.48
Cyclohexene	11.47	3.63	4.58	2.55	1.12	4.45	1.41	1.78	0.99	0.44
2,2,4-Trimethylpentane (Iso-octane)	26.12	7.15	2.29	5.24	2.21	15.17	4.15	1.33	3.04	1.28
2,3,4-Trimethylpentane	20.75	6.26	5.31	4.30	1.84	11.93	3.60	3.05	2.47	1.06
2,3,3-Trimethylpentane	15.24	2.39	2.74	0.00	1.28	8.89	1.39	1.60	0.00	0.75
m-Xylene	37.62	15.99	4.30	8.73	6.61	11.29	4.80	1.29	2.62	1.98
p-Xylene	13.66	8.91	0.00	0.00	0.00	4.12	2.69	0.00	0.00	0.00
o-Xylene	12.02	6.52	0.71	1.87	0.55	3.63	1.97	0.21	0.57	0.17
Formaldehyde	2164.59	1018.52	269.60	277.85	239.24	629.70	296.30	78.43	80.83	69.60
Acetaldehyde	18.16	19.93	6.35	4.03	4.06	7.14	7.83	2.50	1.58	1.59
Acrolein	272.36	2.78	1.20	1.22	1.08	103.79	1.06	0.46	0.46	0.41
2-Butanone (MEK)	40.20	1.22	0.53	0.00	0.08	18.74	0.57	0.25	0.00	0.04
n-Hexanaldehydes	0.00	89.33	3.56	1.36	0.00	0.00	34.18	1.36	0.52	0.00