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PAPER TITLE
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Utilizing Intake-Air Oxygen-Enrichment Technology to Reduce Cold-Phase Emissions

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ABSTRACT

Oxygen-enriched combustion is a proven, seriously considered technique to reduce exhaust hydrocarbons (HC) and carbon monoxide (CO) emissions from automotive gasoline engines. This paper presents the cold-phase emissions reduction results of using oxygen-enriched intake air containing about 23% and 25% oxygen (by volume) in a vehicle powered by a spark-ignition (SI) engine. Both engine-out and converter-out emissions data were collected by following the standard federal test procedure (FTP). Converter-out emissions data were also obtained employing the U.S. Environmental Protection Agency's (EPA's) "Off-Cycle" test. Test results indicate that the engine-out CO emissions during the cold phase (bag 1) were reduced by about 46 and 50%, and HC by about 33 and 43%, using nominal 23 and 25% oxygen-enriched air compared to ambient air (21% oxygen by volume), respectively. However, the corresponding oxides of nitrogen (NO_x) emissions were increased by about 56 and 79%, respectively. Time-resolved emissions data indicate that both HC and CO emissions were reduced considerably during the initial 127 s of the cold-phase FTP, without any increase in NO_x emissions in the first 25 s. Hydrocarbon speciation results indicate that all major toxic pollutants, including ozone-forming specific reactivity factors, such as maximum incremental reactivity (MIR) and maximum ozone incremental reactivity (MOIR), were reduced considerably with oxygen-enrichment. Based on these results, it seems that using oxygen-enriched intake air during the cold-phase FTP could potentially reduce HC and CO emissions sufficiently to meet future emissions standards. Off-cycle, converter-out, weighted-average emissions results show that both HC and CO emissions were reduced by about 60 to 75% with 23 or 25% oxygen-enrichment, but the accompanying NO_x emissions were much higher than those with the ambient air.

INTRODUCTION

A significant portion of the total pollutants emitted by light-duty passenger vehicles occurs immediately following the start-up of the engine. During this period, the engine block and exhaust manifold are cold, and the catalytic converter has not yet reached high conversion efficiencies. In general, the catalyst is not fully effective at temperatures below about 250°C for CO and 250 to 340°C for HC emissions conversion [1]. Hence, most CO and HC emissions are emitted during the cold-phase period (bag 1) of the FTP cycle, when the catalyst is at temperatures below its "light-off" temperature. It is a common practice to operate SI engines with richer fuel-air mixtures during initial start-up and warming-up periods for proper operating driveability and acceleration. As a result, there are more unburned and partially burned hydrocarbons and more CO in the exhaust after the start and first 20 s of idling. The NO_x emissions are low but increase significantly when the vehicle is accelerated in the first transient. Therefore, the emission characteristics are influenced by both the engine operating conditions and the heating characteristics of the catalytic converter. In order to meet the California Air Resources Board (CARB) Transitional Low Emission Vehicle (TLEV), Low Emission Vehicle (LEV) and Ultra Low Emission Vehicle (ULEV) standards, substantial reductions in HC and CO emissions during the cold phase of the FTP cycle are required. Similarly, many light-duty passenger cars are required to reduce these emissions to comply with Tier-II (year 2004) standards. This growing concern over start-up/cold-phase emissions has led to significant activity by passenger car manufacturers to develop new emissions treatment techniques.

The exhaust after-treatment methods to reduce cold-phase emissions so far investigated are grouped into three broad categories [1-4]. They are (1) thermal management of the catalytic converter, including low-mass manifolds, double-walled exhaust pipes, electrically heated catalysts, exhaust gas burners, exhaust gas igniters, and insulated converters (with vacuum or refractory materials); (2) placement of the converter closer to the exhaust manifold; and (3) management of the interaction between the hydrocarbons and the catalyst, using hydrocarbon adsorbent or traps in the exhaust. However, durability, fuel penalty, additional capital costs, unwanted heat in the engine compartment, and the complexity of these systems limit their application in vehicles. Controlling the emissions at the source itself (i.e., during combustion) is a potentially attractive alternative. Oxygen-enrichment of intake air can potentially reduce CO and HC emissions from vehicles powered by an SI engine, even during start-up periods. Since oxygen-enrichment of intake air reduces the engine-out emissions rapidly (even when the engine is cold), it helps to minimize the converter limitations during the cold phase and should improve converter efficiency. This method has the advantage of fewer add-on components, lesser mechanical complexities, and an intake that is much easier to modify with respect to the exhaust system. Perhaps this method has an advantage over the "chemical reactor" approach. In the latter approach, an air injection pump is employed in conjunction with the heated catalyst to provide a stoichiometric exhaust gas composition. Unfortunately, the air-injection rate and timing and the electrical heat input to the catalyst have to be varied simultaneously with exhaust flow, and if the air-injection exceeds the light-off time, poor NO_x conversion is expected. On the other hand, the oxygen-enriched intake air system is simple in operation and does not alter the fuel economy, and the power requirement is comparable with that for an air-injection pump [2].

The concept of using oxygen-enriched intake air for SI-engine combustion has been studied by several researchers over the last two decades. The main motivations for oxygen-enrichment in spark-ignition-engine applications are to lower the exhaust emissions and to improve the power density. The earliest attempts at studying oxygen-enriched combustion were made by Wartinbee [5]. This study was undertaken to demonstrate that oxygen-enriched air could provide a lean oxygen-fuel ratio (the alternative was to restrict the fuel flow). Results indicate that, while HC emissions were reduced substantially, the NO increase precluded further study, given the NO control technologies existing in the 1970s. Subsequently, Quader [6] explained the effects of oxygen-enriched air on exhaust emissions and performance of a SI engine with changes in flame temperatures and flame speeds. Willumeit and Bauer [7] observed a lower fuel consumption at leaner oxygen-fuel ratios, lower HC emissions, and higher NO emissions similar to the previous investigations [5,6]. Kajitani et al. [8] examined the in-cylinder reactions by using high-speed spectral infrared digital imaging in an SI engine with oxygen-enriched air and observed increased thermal radiation (due to higher temperature) from the reaction zone throughout the combustion period. Maxwell et al. [9] demonstrated substantial reductions in CO and HC emissions for both gasoline and natural gas as fuels.

Argonne National Laboratory (ANL) has been studying the oxygen-enrichment concept for both diesel and gasoline engine applications for the past several years. Recently, the potential benefits of intake-air oxygen-enrichment in SI-engine-powered vehicles have been reported [10], on the basis of oxygen-enriched air containing 25 and 28% oxygen by volume. Test results indicate that 28% oxygen was the upper limit due to engine knock. Because cold-phase HC and CO emissions accounted for about 60 to 70% of the total exhaust emissions during the FTP cycle [3], a moderate oxygen-enrichment level (23 to 25%) can be used effectively to reduce these emissions.

Although such benefits as lower HC and CO emissions have been demonstrated by several researchers, the increase in NO_x and lack of an economical source of on-line oxygen equipment have prevented any practical application of this concept. Recent progress in the development of oxygen-enrichment devices, such as the permeable oxygen-membrane [11], and newer NO control technologies, such as lean NO_x catalysts [12] and using monatomic nitrogen induced by a pulse arc to remove nitrogen oxides [13], have stimulated renewed interest in this concept. The key to success of a compact oxygen-enriched air membrane device is the identification, development, and fabrication of new membrane materials [14,15] with dramatically improved flux compared to existing materials.

OXYGEN-MEMBRANE DEVICE - The viability of oxygen-enrichment for vehicular applications depends on the availability of a simple, compact mechanical system driven by the engine itself that will economically extract oxygen from the air. In this regard, the membrane separation (permeation) process is promising compared to traditional methods of extracting oxygen from atmospheric air by using cryogenic liquefaction or pressure-swing adsorption techniques. The membrane permeators typically use polymers that are inherently capable of separating components in a gas mixture by their molecular size (due to diffusion effects). Polymeric membranes are formed into thin films or hollow fibers, usually in an asymmetric structure. Figure 1 is an exploded-view drawing of a typical oxygen-enriched-air membrane module. The capability of a given membrane (in terms of throughput capacity and ability to separate the components in a gas mixture) is governed by the membrane properties (permeability and selectivity) and by operating conditions of temperature, differential pressure across the membrane, and percent recovery. The membrane module size depends on the skin thickness of the fibers, cartridge options (arrangement of fibers for best packing density; geometries, such as spiral-wound and hollow-fiber), and mode of operation (vacuum or pressure). The limiting design criteria for development of a membrane for automotive engine applications are membrane module size and power requirement to drive the membrane. ANL has been examining a new family of materials [15] and comparing them to traditional rubbery polymers (silicon rubber) or glassy polymers (ethyl cellulose and polysulfone) for vehicular applications. An approximate design calculation shows that the power required to drive the membrane is as low as 1.8 kW, and the module size is about 0.508 m length and 0.483 m diameter (20 x 19 in.), using perfluorodioxole membrane material, to produce 2832 L/min (100-scfm),

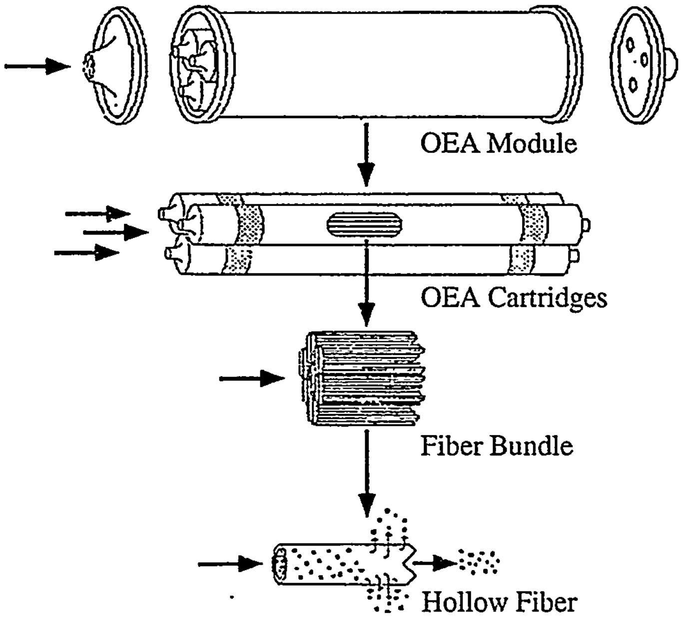

Figure 1. Exploded view of typical oxygen-enriched air module

corresponding to a maximum vehicle speed of 90.93 kmph (56.5 mph) during the FTP cycle, for either 23 or 25% oxygen-enriched air in the (Dodge Spirit, 2.5-L, 75 kW) engine intake. Several design factors are being studied to optimize both membrane size and power requirement. A prototype oxygen-membrane module is under preparation for testing in a vehicle. The mechanism of an oxygen-membrane device to supply oxygen-enriched intake air during the first few minutes after start of the vehicle is currently being developed.

In this paper, results from an SI-engine vehicle using Indolene as a fuel, with intake air containing about 23 and 25% oxygen by volume, are reported. Bottled oxygen was employed to supply 23 or 25% enriched-air during the present tests. Data collected include complete hydrocarbon speciation, mass emissions, and time-resolved (second-by-second) concentrations of HC, CO, and NO_x emissions. A portion of the time-resolved emissions data for the first 127 s of the cold-phase FTP is presented to illustrate the effects of enriched-oxygen in the intake air. A detailed analysis of both engine-out and converter-out emissions has been made, because their relative contributions during this period are significant.

EXPERIMENTAL TEST SET-UP AND PROCEDURE

OXYGEN-ENRICHMENT SYSTEM - The experimental setup was made up of the air-handling and the oxygen-supply systems, as shown in Figure 2. The oxygen-supply system consisted of 12 compressed-oxygen cylinders containing about twice the amount of oxygen required for one FTP emissions test. This system was designed and used for a previous vehicle study [10]. The oxygen-enrichment system used for this study was capable of providing an engine with increasing oxygen concentrations of up to 30% by volume in the intake air. It consisted of a plenum and a blower that provided the plenum with excess air or enriched air for the test vehicle at atmospheric pressure and laboratory air temperature. The intake-air duct of the vehicle was connected to the plenum of the oxygen-enrichment system to provide the vehicle with the required air containing the specified concentration of oxygen for the transient exhaust-emissions test procedures. Additional details about the oxygen-enrichment system are given in Reference 10.

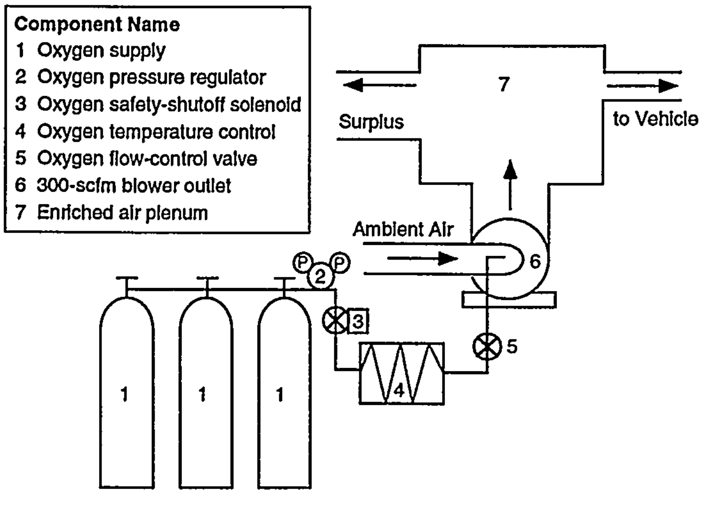

Figure 2. Diagram of oxygen-enriched system

VEHICLE MODIFICATIONS - The vehicle selected for this study was a 1993, M85-Flexible-Fueled Dodge Spirit equipped with a 2.5-L port-fuel-injected engine; the vehicle had an odometer reading of 2490 km. The gasoline used for these tests was Amoco's EPA certification fuel, Indolene. The vehicle was modified for tests using oxygen-enriched air in the same manner used during the previous study [10]. To avoid drawing oxygen-enriched air through the engine crankcase, the PCV system was modified to draw intake air directly from the oxygen-enrichment system to the intake manifold without passing through the crankcase. A PCV valve was installed on the downstream side of the air filter housing and connected to the PCV port on the intake manifold, bypassing the crankcase. The crankcase was then purged by means of a slow flow of nitrogen. The evaporative emissions control (EEC) 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 caused the engine to draw only oxygen-enriched air when the canister purge solenoid was activated, instead of ambient air and fuel vapors. The fuel-tank vapor line was connected to a remote canister. The exhaust system was modified to allow use of either the OEM catalyst to obtain tail-pipe emissions or a simulator converter to obtain engine-out emissions. The simulator converter did contain a briquet without catalyst but was modified to give the same back-pressure as that of an OEM catalyst. Thermocouples were placed in the exhaust line to obtain temperature data before and after the OEM or simulator catalyst. Additional monitoring of the operation of the vehicle during the emissions tests was accomplished by monitoring the regulated emissions concentrations (NMOG, CO, and NO_x), front and rear roll speeds, intake and tail-pipe oxygen concentration, intake air pressure and temperature, and dry and wet-bulb laboratory temperatures on a second-by-second basis.

EXHAUST EMISSIONS TEST PROCEDURE - Both the FTP-75 and one of the EPA's newly developed "Off-Cycle" (REP05) exhaust emissions tests were conducted in duplicate. The two exhaust emissions tests were conducted as specified in the Code of Federal Regulations (CFR) [16], with the exceptions given below:

1. The first test conducted with this vehicle was preconditioned using a modification of the procedure adopted by the Auto/Oil Quality Improvement Research Program (AQIRP) [17]. This procedure involves an evaporative emissions canister purge, fuel flush, diurnal heat-build, 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. The reason for using this preconditioning procedure in this study was to minimize any fuel carry-over and to set the vehicle's adaptive-learning engine control unit (ECU) for the use of emissions certification gasoline.
2. All exhaust emissions 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 emissions canister was eliminated from the intake-air system of the engine.
4. A single LA4 preconditioning cycle was run to condition the vehicle before conducting the first set of FTP and "Off-Cycle" tests at a specified oxygen concentration. For

subsequent tests at the same oxygen concentration, preconditioning was not carried out, because the effect of the evaporative emissions canister was eliminated from this study.

5. The "Off-Cycle" emissions tests were conducted using the EPA's REP05 driving schedule, as shown in Figure 3. These tests were conducted immediately after the FTP test, with the first 505 s of FTP driving cycle used as an engine warm-up procedure.

In addition to the FTP and "Off-Cycle" tests, an additional FTP was conducted to collect regulated and speciated emissions data during only the first 127 s of the cold-phase FTP, using nominal 21, 23, and 25% by volume oxygen concentrations for the intake air of the vehicle. The first 127s of the FTP includes the engine start, 20 s idle, and the first "hill" (cycle) of the test.

SPECIATION ANALYSES - Complete speciation of hydrocarbons, aldehydes, and ketones 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 emissions test. Hydrocarbon speciation of each sample was conducted using gas-chromatographic methodology to quantitatively identify more than 200 hydrocarbons. 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 high-performance liquid chromatography. Additional details of the speciation procedures used are given in Reference 17. The data were reported in terms of milligrams per bag and milligrams per mile for each phase of the FTP emissions test for each compound, in addition to the total weighted grams per mile. In order 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 the aldehyde/ketone cart.

RESULTS AND DISCUSSION

ENGINE-OUT FTP EMISSIONS - The engine-out exhaust emissions during the FTP cycle, with two different oxygen-enrichment levels (nominal 23 and 25%), are presented in Figure 4. Both HC and CO emissions were considerably reduced over the entire FTP cycle, whereas NO_x emissions were relatively higher with oxygen-enriched air compared to ambient air. The variations of HC, CO, and NO_x emissions characteristics with oxygen-enriched intake air were significant, in particular during cold-phase (bag 1) of the FTP test cycle. The percent reductions in HC emissions were about 33 and 43% with 23 and 25% oxygen-enriched air, respectively. In the case of CO emissions, the reductions were much greater than for HC, about 46 and 50% with 23 and 25% oxygen-enriched air, respectively. However, the corresponding NO_x emissions were higher by about 56 and 79%. An increase in oxygen level from 23 to 25% resulted in marginal additional reductions in HC and CO but greater increases in NO_x emissions.

Increasing the oxygen content in the engine intake air from 21 to 23 or 25% by volume decreased HC and CO emissions and increased exhaust NO_x, as was the case with many previous investigations [5-10]. These effects were postulated as a result of the more complete combustion and higher flame temperatures that occur in the presence of oxygen-enriched air. With oxygen-enriched inlet air, more oxygen is made available for oxidation reactions, both in the combustion chamber and in the exhaust. Furthermore, it permits relatively leaner operation, and oxygen-fuel ratios are much closer to stoichiometric, even during the cold-start and warm-up periods. It is expected that the reaction rate will be higher in the combustion chamber with an oxygen-enriched charge, which helps to oxidize the fuel more rapidly. This leads to smaller amounts of unburned HC and CO emissions. The higher flame temperatures and/or flame speeds with oxygen-enriched air are also a cause of lower unburned HC and CO

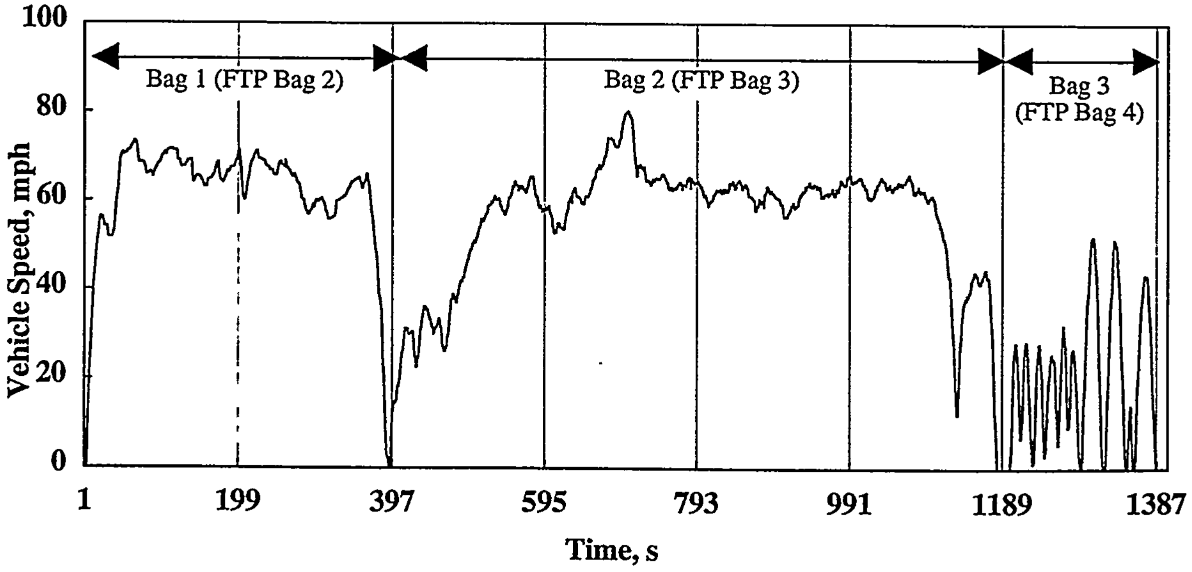

Figure 3. "Off-cycle" test (EPA-REP05)

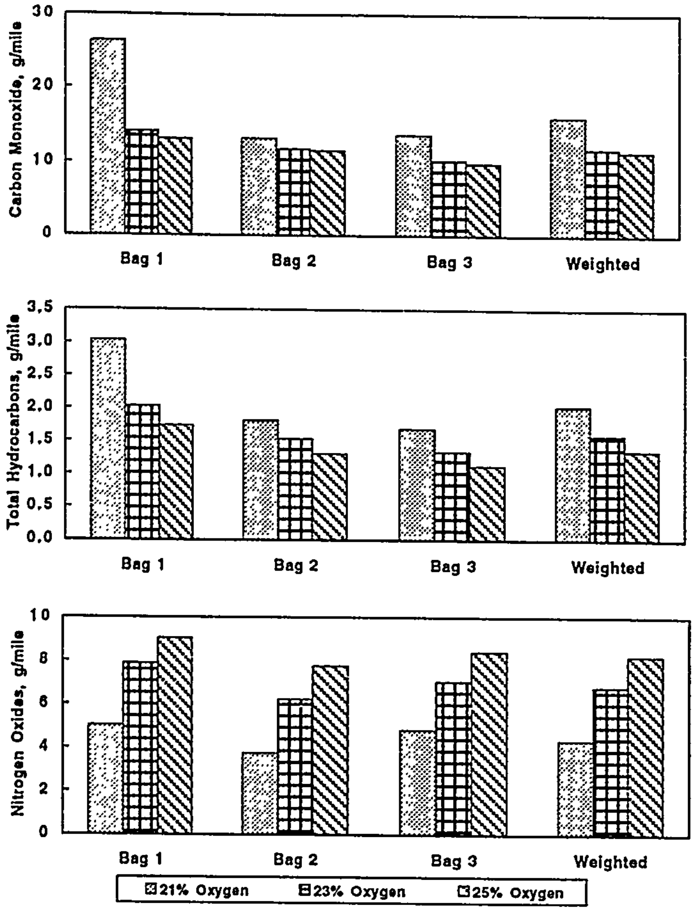

Figure 4. Engine-out exhaust emissions: FTP cycle with indolene fuel

emissions leaving the engine. Increasing oxygen-enrichment increases the flame temperature, with the highest temperature at any given oxygen level occurring near the stoichiometric mixture [6]. Higher flame temperatures have been shown to decrease flame-quenching. Consequently, the HC emissions that originate from flame-quenching effects are decreased by oxygen-enrichment. Moreover, the higher combustion and exhaust gas temperatures may promote post-flame HC oxidation, which may be an additional cause for the observed decrease in HC emissions. All the above-mentioned factors substantiate the observed lower HC and CO emissions using oxygen-enriched air (up to 25% by volume) in the engine inlet air.

The most important engine variables that affect NO emissions are the oxygen-fuel ratio, the burned-gas fraction of the in-cylinder unburned mixture, spark timing, and spark advance. Oxygen-fuel ratio and spark timing interact predominantly to cause the high NO_x emissions with oxygen-enriched inlet air [18]. Oxygen-enrichment causes higher flame temperatures, faster flame speeds (shorter combustion duration), and higher concentration of oxygen in the reacting mixtures, which increases the rate of NO formation. The increase in NO_x level was evident from the observed results (Figure 4). Neither spark timing nor the ECU calibration was optimized in the present oxygen-enrichment experiments. Hence, recalibration of the ECU for proper air/fuel management and spark timing [19,20] to account for the oxygen-enriched inlet air might help to lower the increase in NO_x emissions, and it is essential in reducing all the exhaust emissions simultaneously and effectively. The use of exhaust gas recirculation would reduce NO. However, this is somewhat akin to adding back the nitrogen eliminated through oxygen enrichment.

In order to examine the effect of oxygen-enrichment of intake air on cold-phase FTP exhaust emissions, the emissions characteristics for the initial 127 s during the start-up period were studied in detail, since the majority of the HC and CO emissions are emitted during this period. The vehicle speed during the initial 127 s of the cold-phase FTP (first "hill" or cycle) is shown in (modal analysis) Figure 5. In general, with ambient intake air, CO emission starts increasing from the key-on and reaches its first peak during the engine idle period (about 17 s from the startup). The maximum CO level is reached around the first acceleration peak of the vehicle, and subsequent peaks are synchronized with vehicle acceleration. On the other hand, the first peaks of HC and NO_x emissions appear at about 8 and 30 s, respectively, from key-on. All three emissions reach their maximum values within 24 to 30 s after key-on. During the initial 127-s period, about five to six peaks of both HC and CO emissions, which are predominant contributors to the cold-phase emissions, were significantly reduced with oxygen-enrichment, as illustrated in Figure 6. For example, the first and third peaks, about 850 and 1040 ppm, of HC emissions were reduced to 250 and 540 ppm, respectively, with 25% oxygen-enriched air. The maximum peak of CO, about 7640 ppm, was lowered to about 4100 and 3090 ppm with 23 and 25% oxygen-enriched air, respectively. The corresponding NO_x peak was increased from about 130 to 400 ppm when the oxygen level increased from ambient to either 23 or 25%. Between the 23 and 25% oxygen-enrichment levels, the reduction in CO emissions was considerable at 25%, but marginal in HC emissions. On the other hand, NO_x emissions were higher (a two-fold increase) with increased oxygen level compared to those for ambient air. However, the cold-phase NO_x emissions account for only about 20 to 30% of the total exhaust NO_x, so the increase in NO_x with oxygen-enriched air during the initial 127 s of the cold phase should pose less of a problem if this technique is used only during the cold phase or initial 127 s of the cold-phase FTP cycle.

The major engine-out hydrocarbon compounds such as aldehydes, aromatics, paraffins, and olefins from the hydrocarbon speciation analysis are presented in Figure 7. Aldehydes contribute significantly to ozone formation and in addition to their harmful health effects, they also smell bad. The olefins are also believed to contribute significantly to ozone formation and photochemical smog; particularly such reactive species as ethene, propene, propadiene, isobutene, 2-methyl-1-butene, isoprene, and 1,3-butadiene. Aromatics and paraffins are generally difficult to convert into more harmless species, or eventually into carbon dioxide and water at the catalytic converter. It will be beneficial if the engine produces only small amounts of aromatics and olefins. Among the exhaust hydrocarbon compounds, acetaldehyde, formaldehyde, benzene, and 1,3-butadiene are specifically regulated toxics. Based on the present investigations, oxygen enrichment of the intake air seems to have the capability of decreasing the engine-out concentrations of these difficult-to-oxidize species. From the test results (Figure 7a), we observed that the aldehyde emissions were considerably reduced with oxygen-enriched (23%) air, in particular during the cold phase of the FTP cycle. With 23% enriched oxygen, the reduction in aldehyde emissions was significant; however, with 25%

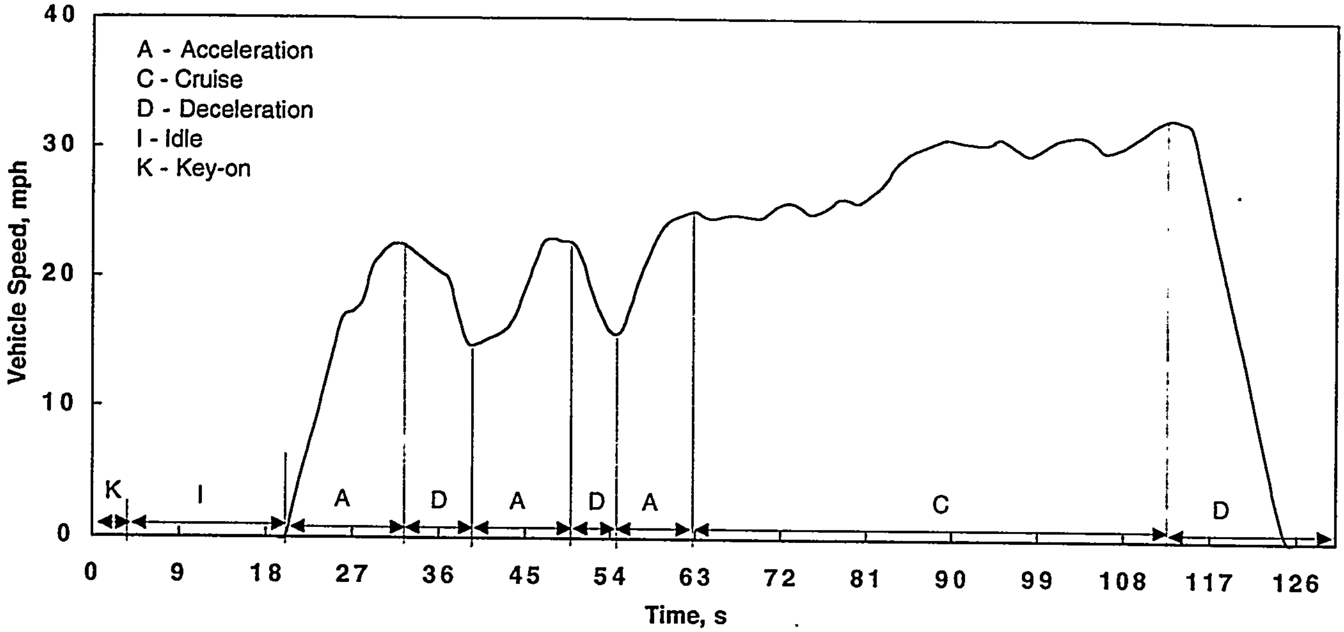

Figure 5. Vehicle speed during first 127 s of the cold-phase FTP

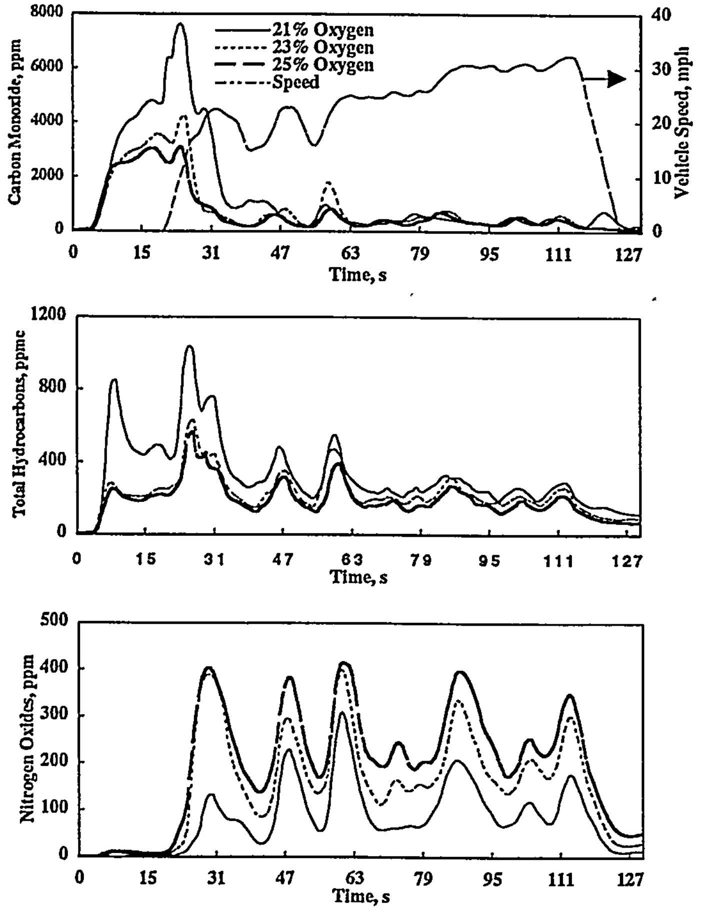

Figure 6. Engine-out time-resolved CO, HC, and NO_X emissions during first 127 s of cold-phase FTP test

enriched oxygen, the percent reduction was less than that obtained with 23%. Probably in the presence of higher oxygen levels, new aldehydes are formed from other previously benign compounds. The mechanism involved in optimizing the level of oxygen-enrichment required to achieve the lowest possible aldehyde emissions is not clear. Of the two different oxygen enrichment levels, 23% is more beneficial with regard to aldehydes, aromatics, some of the paraffins, and olefin emissions, as shown in Figures 7(a) through 7(d).

Of the six major air pollutants for which National Ambient Air Quality Standards (NAAQS) have been listed under the Clean Air Act (CAA), the most pervasive problem continues to be ozone. It is the most prevalent photochemical oxidant and an important component of "smog." Accordingly, ozone has been identified in the CAA as a common and widespread air pollutant [21]. The MIR and MOIR estimate the ozone-forming reactivity of individual compounds under different atmospheric conditions, when limited by the availability of hydrocarbons and NO_x to HC ratio, respectively [22]. These factors are measured in units of grams of ozone per grams of non-methane organic gas (NMOG) in the exhaust. From the light-duty passenger vehicles, the total hydrocarbons emitted are highest during the cold phase FTP. Consequently, both MIR and MOIR factors are of greater significance during this period. Oxygen enrichment changes the composition and also lowers the amount of the hydrocarbons emitted, so that the specific reactivities of ozone formation are lowered with oxygen-enriched air. The reductions obtained in the specific reactivities (MIR and MOIR factors) with 23 and 25% oxygen-enriched air are shown in Figure 7(e).

From the above results, it is observed that oxygen enrichment significantly lowers the engine-out HC and CO, major toxic species, and specific reactivity factors for ozone formation, particularly during the cold-phase FTP. These benefits are realized at the expense of NO_x penalty. Because the converter is generally not fully effective during the initial cold-phase period, the advantages of oxygen-enriched air can be effectively exploited during this period. The oxidation/reduction reactions in the catalyst bed might also be affected due to the change in the engine-out exhaust concentration and temperature with oxygen enrichment. The

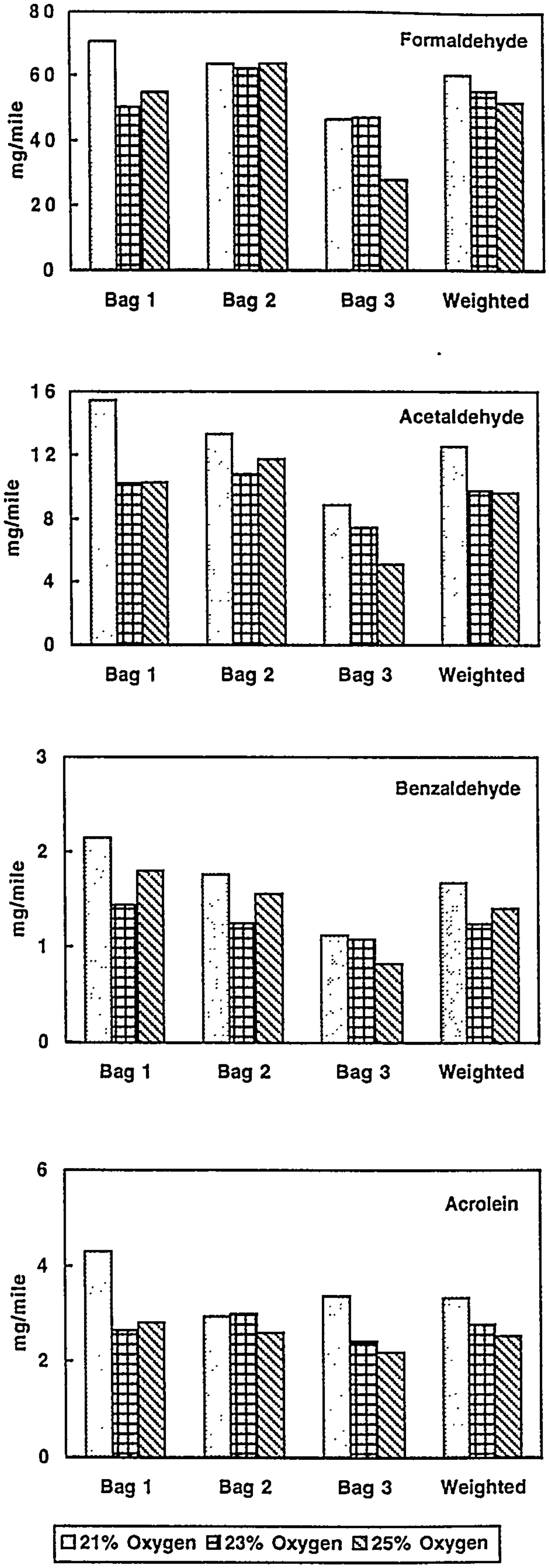

Figure 7(a). Engine-out aldehyde emissions

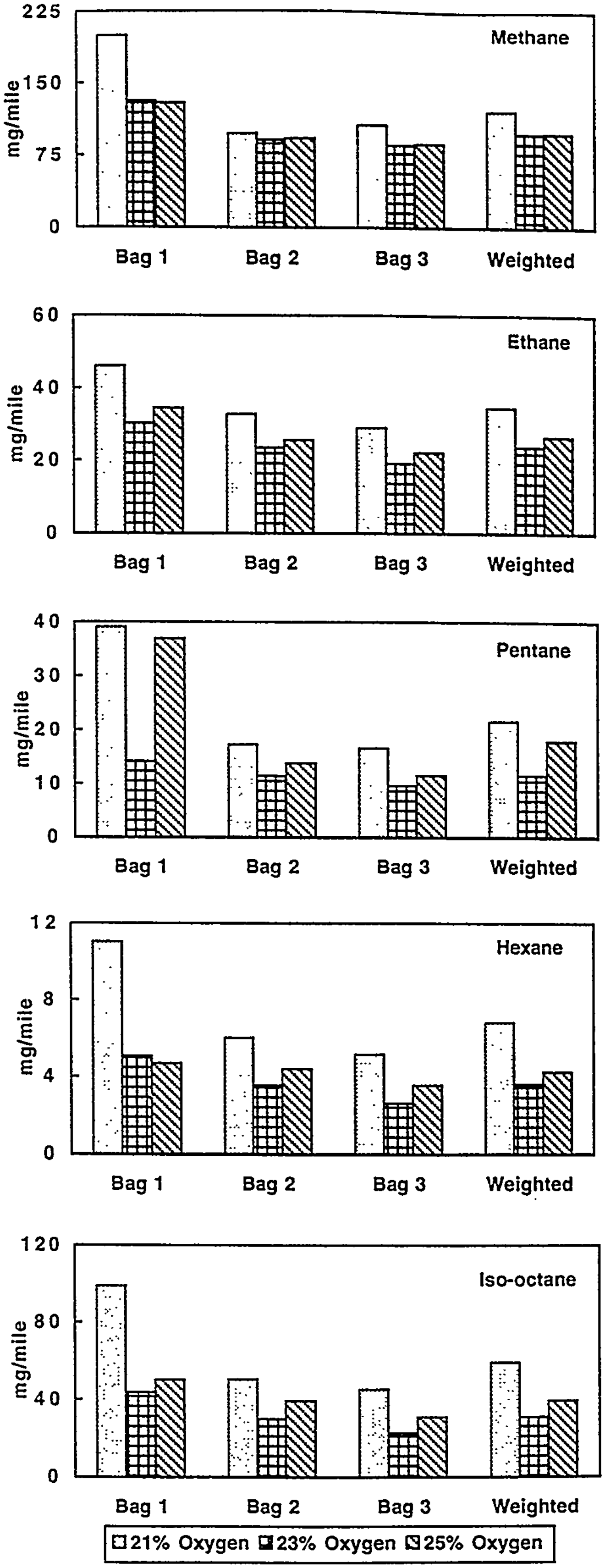

Figure 7(b). Engine-out paraffin emissions

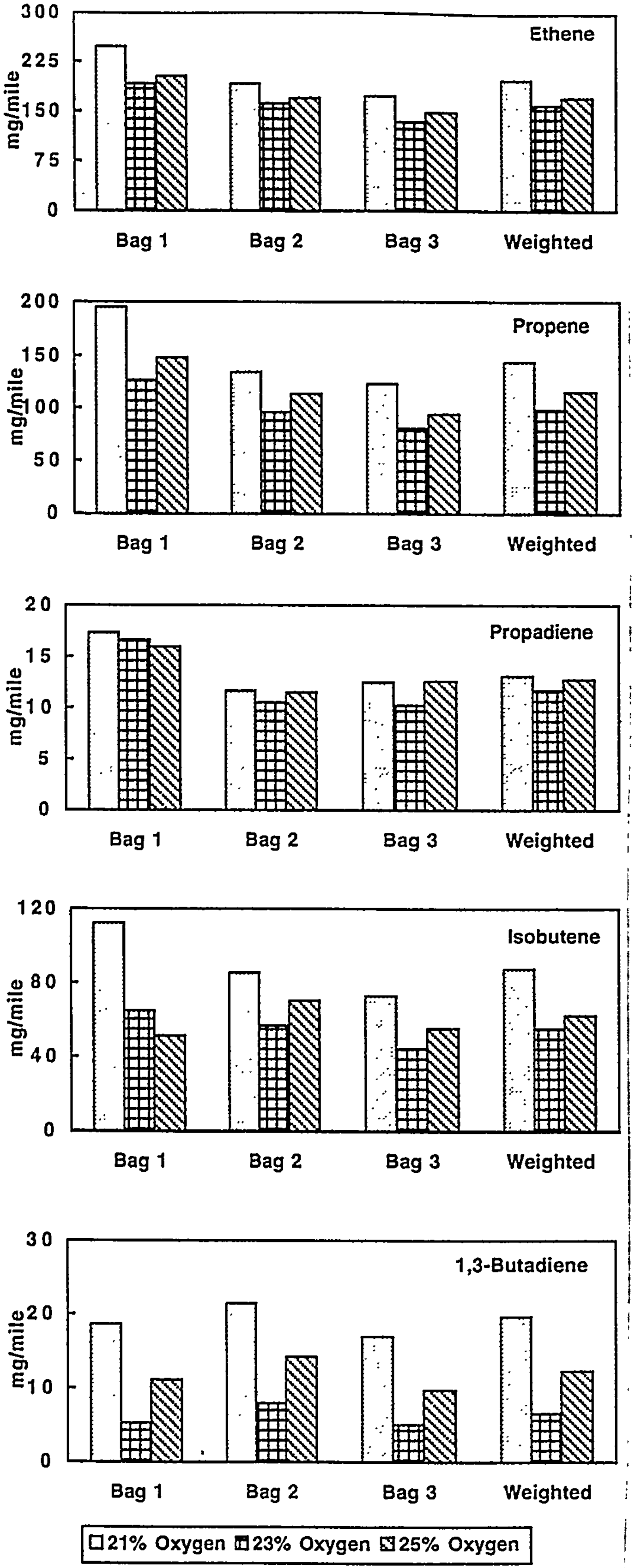

Figure 7(c). Engine-out olefin emissions

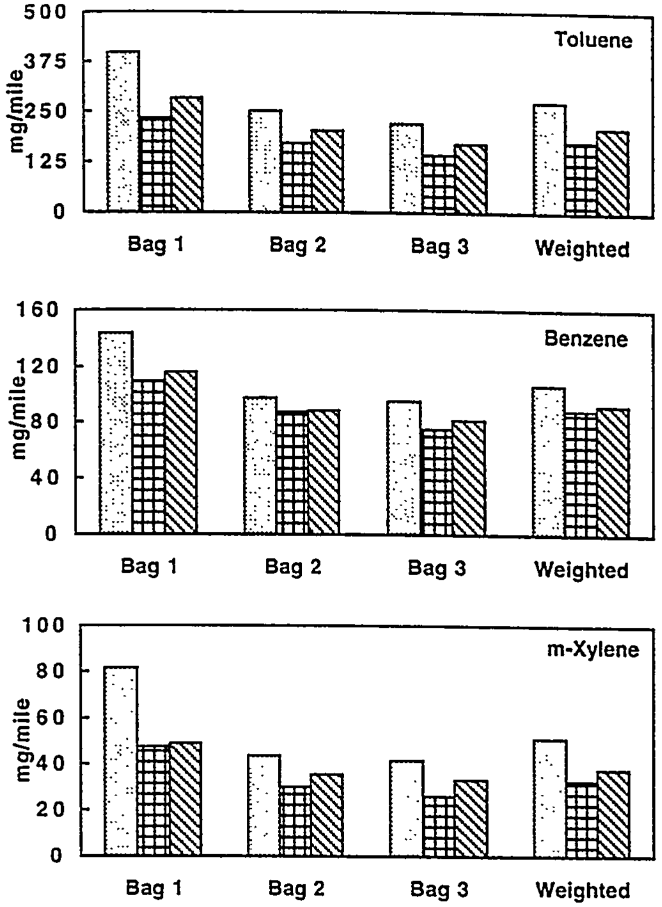

Figure 7(d). Engine-out aromatic emissions

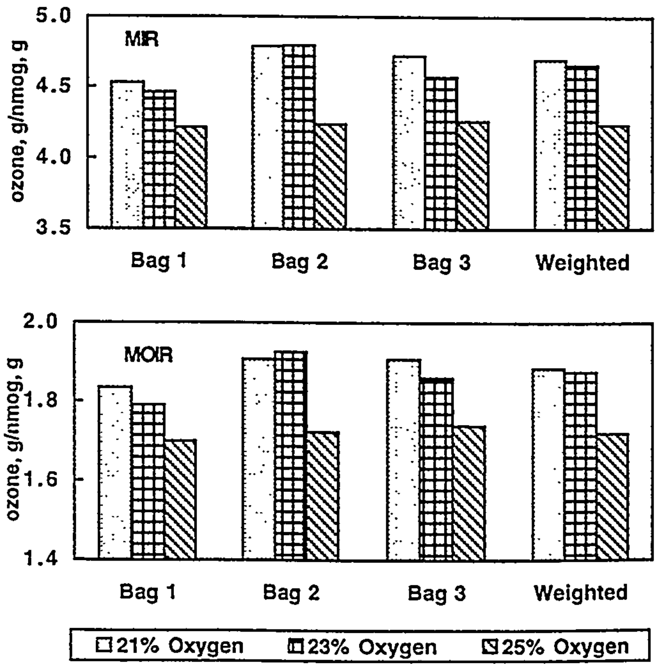

Figure 7(e). Engine-out ozone emissions

following section presents the results obtained from the converter-out emissions with two different oxygen-enrichment levels. The converter-out emissions data presented are the averages of three separate FTP tests performed under similar operating conditions.

CONVERTER-OUT FTP EMISSIONS - Figure 8 shows the average converter-out HC, CO, and NO_x emissions during the FTP cycle with two different oxygen-enriched air levels. Both HC and CO emissions were monotonically reduced with oxygen-enriched air during the entire FTP cycle; this reduction was quite significant at the higher oxygen-enrichment level (25%). The reductions in HC and CO emissions were considerable during the cold phase (bag 1) of the FTP cycle with 23 or 25% oxygen-enriched air. During the cold phase, HC emissions were reduced by about 16 and 30% with 23 and 25% oxygen-enrichment levels, respectively. The corresponding CO emissions were reduced by about 14 and 37%. However, NO_x emissions were higher by about one to three times compared to those obtained with ambient air. The reductions in converter-out emissions are similar to those observed with engine-out emissions. The reductions in converter-out HC and CO emissions are primarily due to lower engine-out emissions resulting from more complete combustion with oxygen-enriched air. Apparently, the additional oxygen available in the engine-out exhaust provided more oxygen for the catalytic oxidation of the CO. In addition, there were substantially fewer hydrocarbons to compete with carbon monoxide for the oxygen. These factors might have influenced the CO oxidation process in the converter.

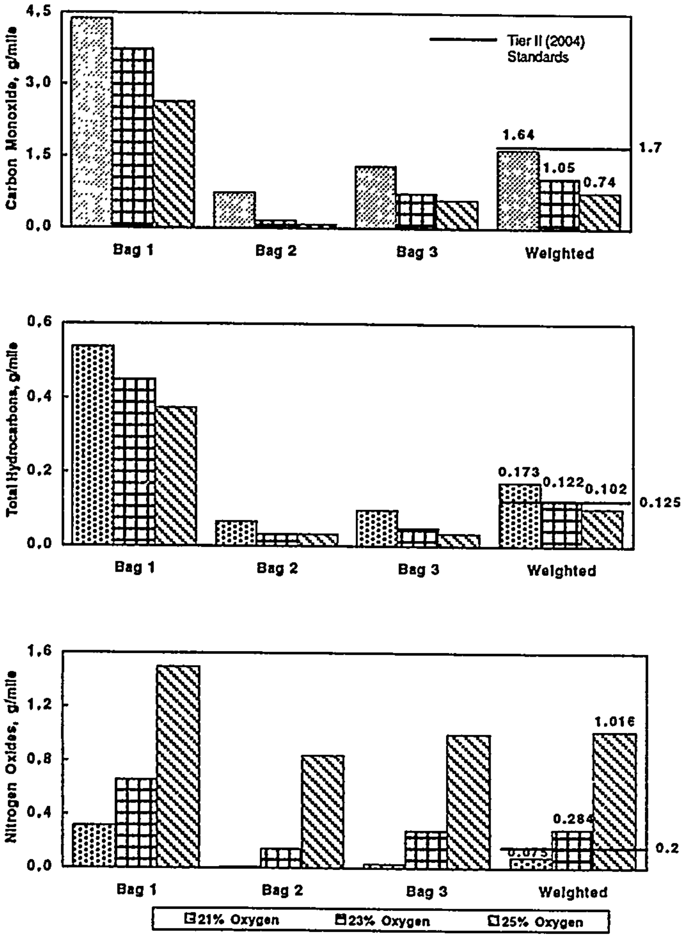

Figure 8. Converter-out exhaust emissions: FTP cycle with Indolene fuel

A comparison of the converter-out emissions obtained with oxygen enrichment with emissions standards for light-duty vehicles for the year 2004 (Tier II) is illustrated in Figure 8. In the present experiments, the vehicle was driven only about 3220 km. Results indicate that, with 25% oxygen-enriched air, the HC and CO emissions were about 18 and 56% lower than the Tier II standards, respectively. In the absence of deterioration factors, it is difficult to assess the benefits of oxygen enrichment after the vehicle operation of 80,467/160,934 km (50,000/100,000 miles). However, it is expected that engine operation with oxygen-enriched air (23 or 25%) would result in lower HC and CO emissions regardless of the vehicle mileage, because adding oxygen-enriched air basically reduces the engine-out emissions. Therefore, conceptually, it has a potential to meet the Tier II standards of HC and CO emissions. The increase in NO_x emissions with oxygen enrichment in the inlet air can be reduced to a certain extent by proper control of spark timing and re-calibration of ECU to account for increased oxygen concentrations. However, with 25% oxygen-enriched air, a post-treatment NO_x control device, such as lean NO_x catalyst or monatomic nitrogen induced by a pulsed arc NO_x control device [13], might be required to comply with the emissions standards. Similarly, 23 or 25% oxygen-enriched air has the potential to meet the TLEV standards with regard to HC and CO emissions but requires a device for additional control of NO_x emissions.

The time-resolved emissions during the initial 127 s of the cold-phase FTP cycle with 23 and 25% oxygen-enrichment levels are presented in Figure 9. Noticeable reductions were obtained by using 25% oxygen-enriched air, compared to the 23% oxygen level, for both HC and CO. For the initial 30 s, 25% oxygen-enriched air was more effective in lowering the first peak of the HC and CO than was the 23% oxygen level; thereafter, both the 23 and 25% levels had similar effects compared to ambient air. The emissions of NO_x were generally higher with either 23 or 25% oxygen-enrichment levels. However, during the initial 25-s period, the NO_x emissions did not increase with either the 23 or 25% oxygen level. Thereafter, they increased with increasing oxygen level. All three types of emissions (CO, HC, NO_x) reached their maximum values within 22 to 27 s from key-on during the first 127-s cold phase period. With 25% oxygen-enriched air, the maximum CO concentration decreased from about 2320 to 1550 ppm, HC decreased from 580 to 400 ppm, and NO_x increased from 180 to 420 ppm when compared to ambient air.

The initial 127-s period of the cold phase is crucial for the catalytic converter because of delay time involved in the catalyst light-off temperature. The time for the heated oxygen sensor to reach operating condition is about 30 s. Thereafter, the engine can be run at stoichiometric mixture, provided driveability is acceptable [2]. Oxygen-enriched intake air helped to lower the engine-out HC and CO emissions during this period. It also helped to increase the converter efficiency, in particular HC and CO conversions, due to the relatively higher oxygen concentration in the exhaust. The relatively higher oxygen level in the exhaust could indirectly help the catalyst to reach its light-off temperature much faster while promoting more oxidation reactions with relatively higher

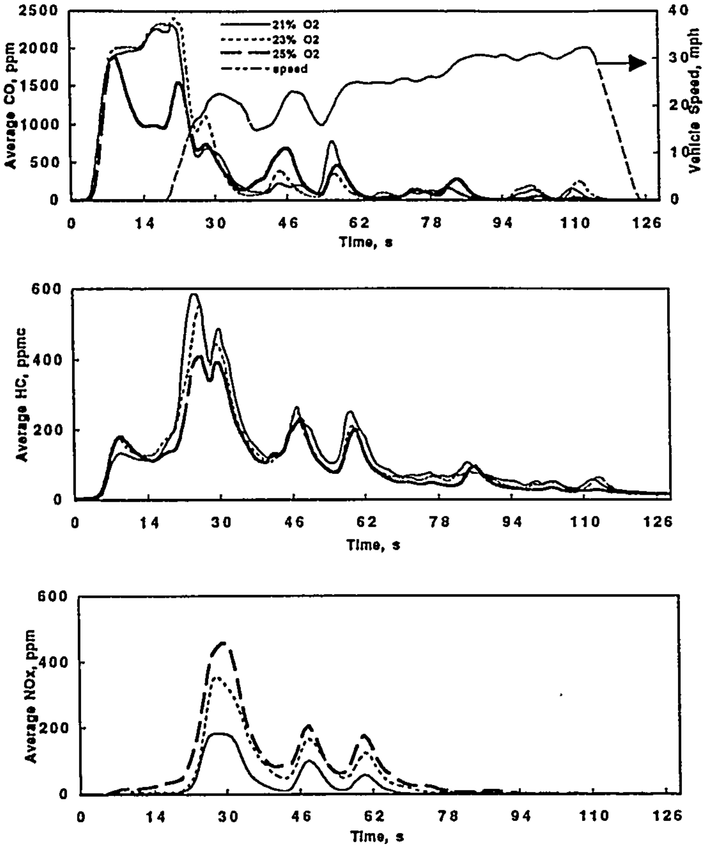

Figure 9. Converter-out time-resolved emissions during first 127 s of cold-phase FTP

exhaust gas temperatures. Catalyst bed temperature measurement (beyond the scope of the present work) would be beneficial to identify the precise time required to reach light-off temperature with and without the oxygen enrichment. The benefits with oxygen enrichment might also vary based on the light-off temperature characteristics of the converter. A converter with inherently longer light-off time might benefit most from the oxygen-enriched inlet air.

The amounts of individual hydrocarbon compounds emitted in the exhaust differed considerably. The CARB has assigned high reactivity factors [22] for certain compounds based on their ozone formation tendency. Hence, there are certain hydrocarbon compounds for which mass emissions are high but their assigned reactivity factors are low, and vice versa. If both mass emissions and corresponding reactivity factors are high, the resultant ozone-forming potential is also high, and these compounds contribute significantly to overall ozone formation. Of the more than 200 hydrocarbon compounds identified quantitatively from the hydrocarbon speciation analysis, about 40 such compounds are considered major contributors (high specific reactivities) to ozone formation. When oxygen-enriched intake air was employed (either 23 or 25%), concentrations of all these compounds were considerably reduced due to lower mass HC emissions. The reductions obtained in ozone-forming potential (based on MIR and MOIR factors) for both engine-out and converter-out using 23 and 25% oxygen-enriched air during the cold-phase FTP are provided in the Appendix.

The effect of oxygen-enriched intake air during the cold phase FTP is also apparent from both the engine-out and converter-out cumulative HC and CO emissions. A comparison of cumulative HC and CO emissions between the trials run using ambient air and those run using 25% oxygen enrichment during the cold-phase FTP is shown in Figure 10. With ambient air, the cumulative engine-out HC and CO emissions increased continuously over the cold-phase period, and cumulative converter-out emissions continued to increase rapidly until >300 s before they leveled off. In contrast, the cumulative engine-out HC and CO emissions with 25% oxygen-enriched air are much lower than those obtained using ambient air. With 25% oxygen-enriched air, the converter-out HC emissions tended to level off much earlier and, at around 130 s and thereafter, the increase in cumulative HC emissions was very marginal. Similarly, the cumulative converter-out CO emissions leveled off at around 90 s with 25% oxygen-enriched air compared to about 300 s with ambient air. These benefits were obtained because of the lower engine-out emissions made possible with oxygen-enriched air. The differences in cumulative emissions of both engine-out and converter-out over time further demonstrate the reductions obtained in HC and CO with oxygen enrichment; in particular, during the cold-phase FTP.

OFF-CYCLE EMISSIONS - The off-cycle test is one of the various federal test cycles under consideration by the EPA and CARB for addition of a more severe driving cycle to the FTP (referred to as "bag 4" cycle [4]). The purpose of this additional driving cycle is to check for the reduced use of fuel enrichment at high engine speed/load conditions required by these regulatory agencies. This cycle was developed to

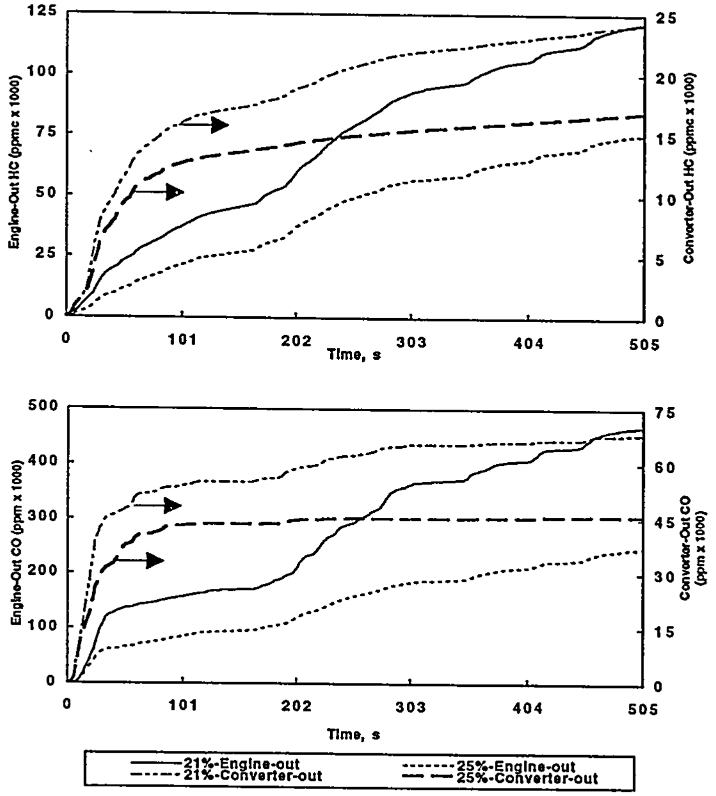

Figure 10. Cumulative engine-out and converter-out average HC and CO emissions during cold-phase FTP

represent in-use driving, which is outside the boundaries of the current FTP driving cycle. The cycle was generated from a composite data set which equally represented Los Angeles chase car data and Baltimore 3-parameter instrumented vehicle data. In the present work, the off-cycle emissions were collected in three different bags, as shown in Figure 3. The off-cycle bag 1 and bag 2 are similar to FTP bag 2 and bag 3 driving cycles. It is clear that off-cycle bag 3 (commonly referred to as bag 4 in the proposed FTP test) consists of rapid accelerations and decelerations for about 200 s in the test cycle. The exhaust emissions from bag 4 of the FTP driving cycle might pose the greatest challenge for the converter, because exhaust emissions increase rapidly in both mass and concentration at higher fuel flow rates. Nevertheless, the potential benefits of intake air oxygen enrichment can be applied to reduce these emissions effectively. The reductions obtained with oxygen-enriched air during the off-cycle test are shown in Figure 11. The converter-out CO emissions during

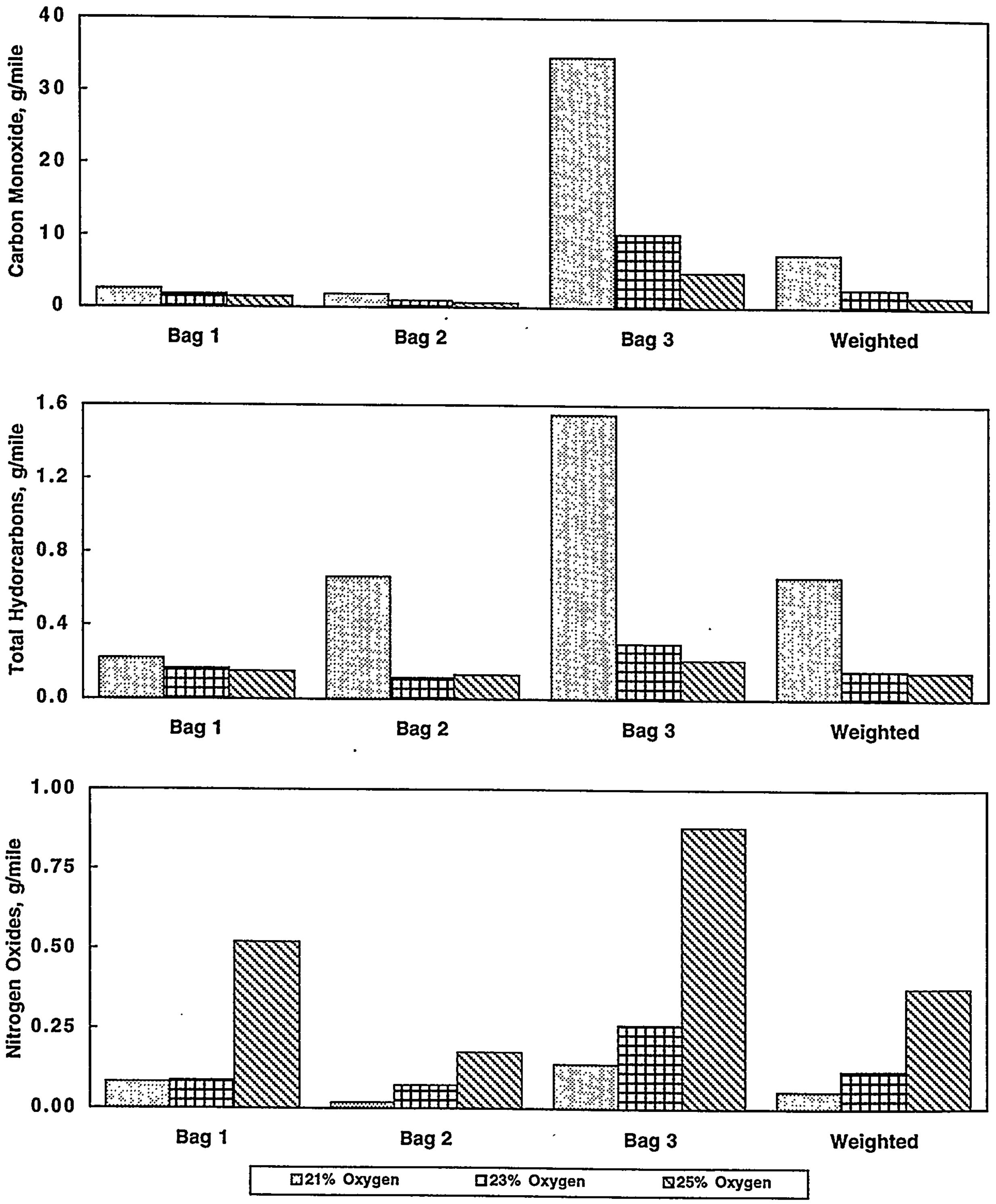

Figure 11. Off-cycle converter-out exhaust emissions with Indolene fuel

the off-cycle bag 3 (bag 4 of FTP) decreased from 34.6 to 13.4 (61%) and 4.7 g/mile (86%) when the oxygen level in the intake air increased from 21 to 23 and 25% respectively, over ambient air. Similarly, HC emissions were reduced from 1.55 to 0.3 (37%) and 0.21 g/mile (57%) by using 23 and 25% oxygen-enriched air, respectively. However, the corresponding NO_x emissions increased from 0.019 to 0.058 and 0.135 g/mile under the same conditions. The weighted-average, off-cycle emissions reductions were promising with oxygen enrichment; NO_x emissions did not increase beyond 0.13 g/mile even with 25% oxygen-enriched air while both HC and CO emissions were very low (about 0.06 and 0.45 g/mile, respectively). In order to control NO_x emissions by using oxygen-enriched air (in particular with 25% oxygen level), such methods as relearning of the ECU, proper air/fuel and spark-timing management, and an additional post-treatment device are required, if bag 3 of the off-cycle is going to be added to the existing FTP test cycle as bag 4. Hence, 23% oxygen-enriched air seems to be a compromise to reduce both HC and CO emissions with less penalty of NO_x emissions during the off-cycle test.

RECOMMENDATIONS

The suitability of a given oxygen-enrichment level for a particular engine depends on the desired reductions of both HC and CO, as well as on simultaneous control of NO_x emissions without exceeding the emissions standards. This can be done in different ways, as listed below:

1. Adding 23% oxygen-enriched air during the entire FTP cycle: In this case, FTP weighted-average emissions of both HC and CO are lower than the Tier II standards, and with proper control of spark timing and ECU calibration, NO_x limits might be attained.
2. Adding 25% oxygen-enriched air during the entire FTP cycle: Both HC and CO are considerably reduced but the increase in NO_x might require additional control devices to comply with TLEV/LEV or Tier II standards.
3. Adding 25% oxygen-enriched air only during the cold phase or initial 127 s of the cold-phase FTP cycle: This method seems to be the most promising approach to reduce cold-phase HC and CO emissions while keeping NO_x emissions sufficiently low by proper control of oxygen-fuel ratio and spark timing.

One method of achieving low NO_x levels while using oxygen-enriched air is to employ a "bag 1 strategy" as described in case 3 above. In this approach, oxygen-enriched air is supplied only during the bag 1 of the FTP cycle. During the bag 2 and bag 3 periods, ambient air is employed. Figure 12 compares both engine-out and converter-out FTP emissions for ambient air and 25% oxygen-enriched air during bag 1. With this technique, the problem of increased NO_x emissions can be alleviated to a certain extent while considerably reducing HC and CO emissions. As a result of the lower cold-phase HC and CO emissions, the FTP weighted-average emissions were also reduced using 25% oxygen-enriched air, as illustrated in Figure 12. A summary of the FTP converter-out emissions results is provided in Table 1 along with different emissions standards. By using 25% oxygen-enriched air with an optimized ECU only during the cold phase or initial 127-s period of the cold phase, there is a good potential to lower all three (HC, CO, NO_x) emissions simultaneously to meet the TLEV/LEV and Tier II standards. Hence, this approach seems to be a more practical way of utilizing oxygen-enriched air to reduce the cold-phase HC and CO emissions with a lower NO_x penalty.

CONCLUSIONS

On the basis of the present investigations on a 1993, M-85-Flexible-Fueled Dodge Spirit with a 2.5-L port-fuel-injected engine, light-duty passenger vehicle utilizing oxygen-enriched intake air to reduce cold-phase FTP emissions, the following conclusions are drawn:

1. Intake-air oxygen enrichment has the potential to reduce both HC and CO emissions, in particular during cold-phase FTP. Oxygen enrichment reduces the engine-out emissions by allowing more complete combustion and higher flame temperatures and, as a result, lowers emissions prior to converter light-off.
2. With 25% oxygen-enriched intake air, the FTP converter-out HC and CO emissions were reduced by about 41 and 55% respectively, over emissions obtained using ambient air. However, NO_x emissions were higher (increased from 0.075 to 1.01 g/mile), which necessitates a post-treatment device and or proper control of spark timing and air-fuel management to account for the increased oxygen level.
3. A modest increase in the oxygen-enrichment level up to 23% can be used in the FTP test cycle to reduce both HC and CO emissions and also to meet the TLEV and year 2004 (Tier II) standards. The increase in NO_x could be manageable with re-calibration of the ECU.
4. The oxygen-enrichment level for a particular engine depends on the desired reductions of both HC and CO emissions and on proper control of NO_x to comply with future emissions standards. The most promising scheme is to use up to 25% oxygen-enriched air only during the cold phase or initial 127 s of the cold-phase FTP. A reduction of about 30 to 40% in the converter-out, bag 1 HC and CO emissions can be achieved by using this "bag 1 strategy."
4. Concentrations of major toxic pollutants and many hydrocarbon compounds contributing to ozone formation (measured in terms of maximum incremental reactivity and maximum ozone incremental reactivity factors) are considerably reduced with 23 or 25% oxygen-enriched air. As a result of lower cold-phase total hydrocarbons using oxygen-enriched air, concentrations of about 40 hydrocarbon compounds that are more likely to form ozone are significantly reduced.
5. Exhaust HC and CO emissions from the bag 3 (FTP bag 4) during EPA's "off-cycle" test are difficult to control using conventional catalytic converters, due to rapid acceleration and decelerations during the driving cycle. However, with moderate oxygen enrichment of intake air (up to 23% oxygen), about 60 to 70% of HC and CO emissions can be reduced. The increase in NO_x due to oxygen enrichment may not pose any problem and may allow manufacturers to meet the emissions standards.

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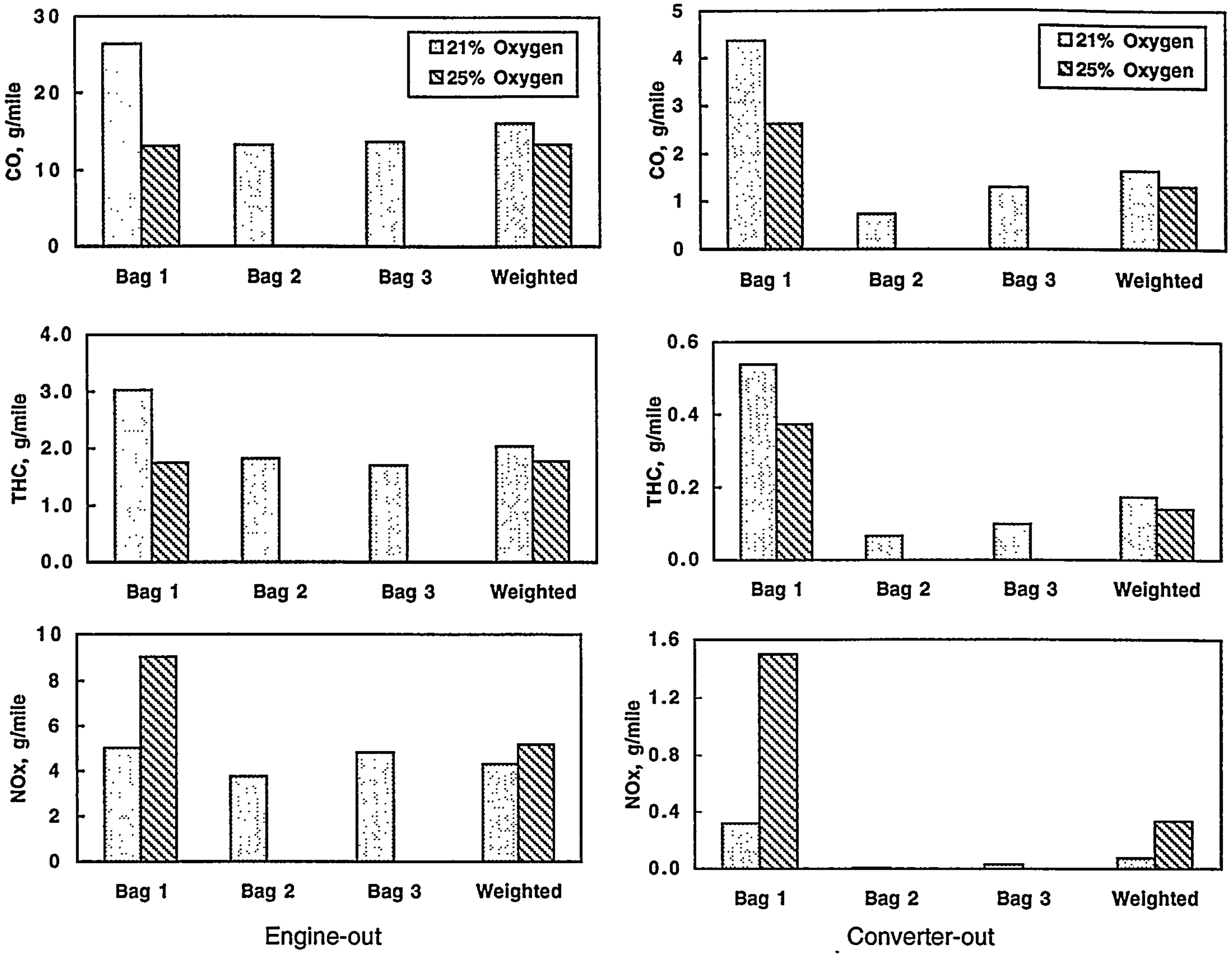

Figure 12. Engine-out and converter-out emissions with 25% oxygen enrichment only during cold-phase FTP

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

	HC	g/mile	CO	g/mile	NO_x	g/mile
Engine Intake	Bag 1	Weighted	Bag 1	Weighted	Bag 1	Weighted
Ambient air	0.538	0.173	4.38	1.64	0.315	0.075
23% Oxygen	0.451	0.122	3.74	1.05	0.655	0.284
25% Oxygen	0.371	0.102	2.63	0.73	1.56	1.01
25% Oxygen cold phase only	0.371	0.141	2.63	1.30	1.56	0.33
Standards @ 0 mileage						
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

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DISCLAIMER

Appendix

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

	mg of ozone/mile (based on MIR)						mg of ozone/mile (based on MOIR)					
	Engine-Out			Converter-Out			Engine-Out			Converter-Out		
Compound Oxygen:	21%	23%	25%	21%	23%	25%	21%	23%	25%	21%	23%	25%
Ethene (Ethylene)	1811.6	1478.3	1394.1	221.7	233.2	208.8	785.3	640.8	604.3	96.1	101.1	90.5
Acetylene (Ethyne)	107.9	81.8	87.4	7.0	8.5	7.3	71.2	54.0	57.7	4.6	5.6	4.8
Propene (Propylene)	1836.2	1389.0	1190.5	239.8	249.4	214.1	736.4	557.1	477.5	96.2	100.0	85.9
Benzene	60.2	48.6	45.9	11.5	10.0	7.8	20.1	16.2	15.3	3.8	3.3	2.6
Toluene	1082.8	771.4	635.8	210.8	183.4	135.8	249.9	178.0	146.7	48.6	42.3	31.3
Methylacetylene (Propyne)	86.8	85.2	90.8	1.4	2.5	4.2	46.0	45.1	48.1	0.7	1.3	2.2
Isobutylene	595.4	272.1	343.2	56.1	81.3	62.2	216.4	98.9	124.7	20.4	29.6	22.6
1,3-Butadiene	203.0	121.1	57.6	43.4	18.2	21.2	77.5	46.3	22.0	16.6	6.9	8.1
n-Butane	22.7	15.1	10.5	20.6	11.6	12.4	14.7	9.7	6.8	13.3	7.5	8.0
trans-Butene-2	122.8	82.4	73.8	21.4	17.3	12.5	46.4	31.2	27.9	8.1	6.5	4.7
cis-Butene-2	101.2	66.4	60.1	11.8	11.3	9.6	38.3	25.1	22.7	4.5	4.3	3.6
Isopentane	668.4	341.7	309.8	162.4	109.4	55.4	250.7	128.1	116.2	60.9	41.0	20.8
2-Methylbutene-1	45.2	22.6	18.6	7.1	5.2	3.4	17.5	8.8	7.2	2.8	2.0	1.3
n-Pentane	40.6	38.4	14.8	9.9	5.0	30.8	26.6	25.1	9.7	6.5	3.7	20.1
2-Methyl-1,3-Butadiene	42.9	18.2	0.9	13.0	11.6	9.4	16.1	6.8	0.3	4.9	4.4	3.5
trans-Pentene-2	50.2	25.5	22.2	7.3	3.8	3.0	18.8	9.6	8.3	2.7	1.4	1.1
2-Methylbutene-2	98.9	45.6	32.6	20.4	15.3	11.4	35.5	16.4	11.7	7.3	5.5	4.1
3-Methylpentene-1	25.4	12.7	11.3	14.0	1.2	0.6	14.1	7.1	6.3	5.3	0.5	0.2
2,3-Dimethylbutene-2	95.4	47.8	42.3	23.4	18.7	12.0	35.6	17.9	15.8	8.7	7.0	4.5
Cyclohexene	117.7	57.3	50.3	30.1	22.8	14.6	45.7	22.2	19.5	11.7	8.8	5.7
2,2,4-Trimethylpentane	92.2	46.8	41.0	23.4	18.7	11.9	53.5	27.2	23.8	13.6	10.9	6.9
2,3,4-Trimethylpentane	71.7	35.8	30.5	18.7	14.6	9.2	41.2	20.6	17.6	10.7	8.4	5.3
2,3,3-Trimethylpentane	79.2	31.0	4.0	10.1	8.2	3.2	46.2	18.1	2.3	5.9	4.8	1.8
Ethylbenzene	139.4	81.1	73.8	15.2	20.7	14.5	32.5	18.9	17.2	3.6	4.8	3.4
m-Xylene	664.1	399.7	389.6	95.8	97.8	70.6	199.4	120.0	117.0	28.8	29.4	21.2
p-Xylene	291.5	175.0	155.6	43.2	35.1	26.6	87.9	52.8	46.9	13.0	10.6	8.0
o-Xylene	191.8	120.3	108.5	43.6	30.7	22.0	57.9	36.3	32.8	13.2	9.3	6.6
n-Propylbenzene	25.5	12.0	10.3	2.9	3.4	1.9	5.9	2.8	2.4	0.7	0.8	0.4
3-Ethyltoluene	361.4	193.4	162.4	45.1	52.8	36.4	108.4	58.0	48.7	13.5	15.9	10.9
4-Ethyltoluene	157.6	83.8	70.6	19.5	24.0	15.7	47.3	25.1	21.2	5.8	7.2	4.7
1,3,5-Trimethylbenzene	252.5	144.2	122.6	50.7	40.5	27.2	76.1	43.5	36.9	15.3	12.2	8.2
2-Ethyltoluene	122.0	67.0	53.4	9.3	12.8	12.1	36.6	20.1	16.0	2.8	3.8	3.6
tert-Butylbenzene	72.0	39.2	31.7	14.4	12.1	8.3	16.6	9.0	7.3	3.3	2.8	1.9
1,2,3-Trimethylbenzene	150.3	79.2	66.7	11.6	20.8	11.8	45.3	23.9	20.1	3.5	6.3	3.6
Formaldehyde	505.9	392.1	359.8	29.6	27.0	26.4	147.2	114.1	104.7	8.6	7.9	7.7
Acetaldehyde	85.2	56.9	56.5	13.3	14.1	13.1	33.5	22.4	22.2	5.2	5.6	5.1
Acrolein	29.0	19.0	17.9	2.1	2.0	2.2	11.1	7.2	6.8	0.8	0.8	0.8