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Potential Benefits of Oxygen-Enriched Intake Air in a Vehicle Powered by a Spark-Ignition Engine

by H.K. Ng and R.R. Sekar

Center for Transportation Research, Energy Systems Division,
Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

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POTENTIAL BENEFITS OF OXYGEN-ENRICHED INTAKE AIR IN A VEHICLE POWERED BY A SPARK-IGNITION ENGINE

by

H.K. Ng and R.R. Sekar

ABSTRACT

A production vehicle powered by a spark-ignition engine (3.1-L Chevrolet Lumina, model year 1990) was tested. The test used oxygen-enriched intake air containing 25 and 28% oxygen by volume to determine (1) if the vehicle would run without difficulties and (2) if emissions benefits would result. Standard Federal Test Procedure (FTP) emissions test cycles were run satisfactorily. Test results of catalytic converter-out emissions (emissions out of the converter) showed that both carbon monoxide and hydrocarbons were reduced significantly in all three phases of the emissions test cycle. Test results of engine-out emissions (emissions straight out of the engine, with the converter removed) showed that carbon monoxide was significantly reduced in the cold phase. All emission test results were compared with those for normal air (21% oxygen). The catalytic converter also had an improved carbon monoxide conversion efficiency under the oxygen-enriched-air conditions. Detailed results of hydrocarbon speciation indicated large reductions in 1,3-butadiene, formaldehyde, acetaldehyde, and benzene from the engine with the oxygen-enriched air. Catalytic converter-out ozone was reduced by 60% with 25%-oxygen-content air. Although NO_x emissions increased significantly, both for engine-out and catalytic converter-out emissions, we anticipate that they can be ameliorated in the near future with new control technologies. The automotive industry currently is developing exhaust-gas control technologies for an oxidizing environment; these technologies should reduce NO_x emissions more efficiently in vehicles that use oxygen-enriched intake air. On the basis of estimates made from current data, several production vehicles that had low NO_x emissions could meet the 2004 Tier II emissions standards with 25%-oxygen-content air. The results indicate that adding oxygen to the intake air, instead of to the fuel (as in oxygenated gasoline), can achieve the same emissions reduction goal.

1 INTRODUCTION

The potential merits of oxygen enrichment in the intake air of spark-ignition engines are still being contested today.¹⁻³ The most recent Japanese study³ showed an increase in

thermal efficiency and a decrease in exhaust emissions of unburned hydrocarbons and carbon monoxide, whereas a General Motors report from 1971¹ had shown decreases in thermal efficiency and decreases in unburned hydrocarbon and carbon monoxide emissions. However, both studies reported a substantial increase in NO_x emissions.

The primary objective of this study was not to resolve the differences in fuel economy, but to determine if a polymeric-membrane oxygen-enrichment system could be readily retrofitted to a vehicle powered by a spark-ignition engine to produce reasonable performance with reduced emissions. Because most vehicles are fitted with three-way catalytic converters, which only work in a reducing environment, this experiment also showed whether this technique would have major impact on converter performance.

Another objective of this study was to determine if the oxygen-enrichment process would change some of the many hydrocarbon oxidation processes in the combustion chamber and the numerous catalytic hydrocarbon reactions in the converter and, consequently, modify the composition of exhaust hydrocarbons. In addition, the amount of benzene, 1,3-butadiene, formaldehyde, and acetaldehyde in the exhaust emissions was measured. [These constitute four out of the five air pollutants designated as toxic by the 1990 Clean Air Act (CAA).]

In this experimental study, intake-oxygen contents of 21, 25, and 28% were used in a production Chevrolet Lumina for emissions testing under the Standard Federal Test Procedure (FTP), 40 Code of Federal Regulations (CFR), Part 86. Both the engine-out emissions and the catalytic converter-out emissions were measured, and the distribution of hydrocarbon species were measured by means of gas chromatography.

Engine out emissions were emissions that came directly out of the engine (with the converter removed). *Catalytic converter out emissions* were emissions that came out of the catalytic converter (three-way catalytic was attached to the engine). All emission test results were compared with normal air (21% oxygen).

2 EXPERIMENTAL SETUP AND TEST PROCEDURES

2.1 BACKGROUND

To perform the experiment, an oxygen-enrichment system was designed and fabricated. The vehicle chosen, because of its popularity, was a 3.1-L Chevrolet Lumina, model year 1990. A variable-fuel version (VfV) of this vehicle is scheduled to be used for a subsequent, alternative-fuel study using oxygen enrichment. The tests were performed at the AutoResearch Laboratory in Harvey, Illinois.

2.2 OXYGEN-ENRICHMENT SYSTEM

The experimental setup was made up of the air-handling and the oxygen-supply systems, as shown in Figure 2.1. The air-handling system consisted of a plenum and a blower (300 standard ft³/min^{*}) that continuously provided the plenum with excess air. The vehicle drew the intake air as required, and the excess air was purged. This system was designed to handle ambient air (21% oxygen) and up to 30% oxygen-enriched air.

The oxygen-supply system consisted of 12 compressed-oxygen cylinders containing about twice the amount of oxygen required for one FTP emissions test. The outlet 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 bring the oxygen to room temperature. The heated air was then fed into the air-handling system 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 means of a valve 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 a desired oxygen content at the plenum. Once the system stabilized, the emissions test or conditioning cycle would start. Normally, this start-up process would take about 3-5 min.

To demonstrate that the oxygen-enriched-air-handling system would function properly during the FTP emissions test cycle at the four different oxygen contents, the vehicle was driven through the first two hills of the driving cycle. As shown in Figure 2.2, the oxygen contents of 21, 25, 28, and 30% (measured at the plenum) remained fairly stable through these driving sections. (Note: The 30% oxygen concentration was not used in the actual FTP emissions test.)

* scfm = standard cubic feet per minute, ft³/min.

Component Name

- 1 Oxygen supply
- 2 Oxygen pressure regulator
- 3 Oxygen safety-shutoff solenoid
- 4 Oxygen temperature control
- 5 Oxygen flow-control valve
- 6 300-scfm blower outlet
- 7 Enriched air plenum

FIGURE 2.1 Diagram of Oxygen-Enrichment System

Plenum Oxygen Concentrations During First 2 Hills of Constant Volume Sampling Cycle at 4 Levels of Oxygen

FIGURE 2.2 Stability of Oxygen-Enrichment System

The compressed oxygen from the cylinders had the potential of over-pressurizing the air-handling system and feeding the vehicle with excessive oxygen. Therefore, three manually operated emergency shutoff switches were installed, one each in the control panel of the enriched-air-handling system, the emissions lab, and the vehicle.

2.3 VEHICLE MODIFICATIONS

The positive crankcase ventilation (PCV) and the evaporative emissions control (EEC) system on the 3.1-L Chevrolet Lumina were modified for this experiment. To avoid drawing the oxygen-enriched air through the engine crankcase, the PCV was short-circuited. A PCV valve was installed on the downstream side of the air-filter housing and was connected to the PCV port on the intake manifold, bypassing the crankcase. The crankcase was then vented to the exhaust system of the test cell.

The EEC system was modified to bypass 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. During oxygen-enriched-air operation, this modification would cause the engine to draw only the oxygen-enriched air (instead of the ambient air and fuel vapors) when the canister purge solenoid was activated. The fuel-tank vapor line was connected to a remote canister located at the rear of the vehicle. This line could be easily changed when it became loaded with fuel vapor.

For the engine-out emissions tests, the catalytic converter was removed and replaced by a piece of exhaust pipe. The pressure drop across the catalytic converter, however, was not simulated. For the catalytic converter-out emissions tests, the catalytic converter (with about 7,000 mi under normal driving conditions) was reinstalled.

2.4 FTP EMISSIONS TEST PROCEDURES

The vehicle was conditioned for testing by driving a single LA4 cycle (Los Angeles driving cycle #4) while operating at the oxygen content to be tested. Following a 12-h minimum soak period (68-86°F), vehicle exhaust emissions were measured per the FTP specified in 40 CFR, Part 86. Subsequent duplicate tests were separated by a 12-h minimum soak period with no reconditioning. The diurnal heat-build portion of the FTP was not performed because of the modifications made to the EEC system of the vehicle.

Tests were made in three phases: cold phase, stabilized phase, and hot phase. Three different oxygen percentages were used: 21, 25, and 28%. Air bags were used to collect the exhaust emissions for each of the three phases. A separate bag was used for each oxygen enrichment mix (21, 25, and 28%) at each phase. The air bags were labeled as follows:

- Bag 1 (Cold Phase). Includes separate bags for 21, 25, and 28% oxygen enrichment.

- **Bag 2 (Stabilized Phase).** Includes separate bags for 21, 25, and 28% oxygen enrichment.
- **Bag 3 (Hot Phase).** Includes separate bags for 21, 25, and 28% oxygen enrichment.

2.5 HYDROCARBON SPECIATION TECHNIQUES

Hydrocarbon speciation was performed by analyzing a portion of the diluted exhaust sample by means of gas chromatography. One sample was analyzed from each of the three bags of exhaust gas collected for the three phases of the FTP emissions test. Aldehyde levels were measured by passing the diluted exhaust sample through silica gel cartridges impregnated with 2,4-dinitrophenylhydrazine. One cartridge was used for each of the three bags.

3 EXPERIMENTAL RESULTS AND DISCUSSION

3.1 VEHICLE PERFORMANCE

The vehicle ran smoothly with the oxygen-enriched intake air at increasing oxygen content until this content reached 30% by volume; at 30% oxygen, the engine began to knock. Even though the test facility was very noisy, because of the oxygen rushing out of the cylinders, the hammering noise coming from the engine was very noticeable. At and below an oxygen content of 28%, the vehicle had excellent response, and the driver had to back off the throttle to keep the required speed for the FTP emissions tests.

At an oxygen content of 28%, there was no audible knocking throughout the FTP emissions test; however, there was a constant need for timing retardation during acceleration. Timing retardation increased from about 5 crank angle (CA) for 0-30 mph (modest acceleration) to about 11 CA for 0-55 mph (hard acceleration). The output from the knock sensor, in combination with the timing retard record, provided a fair indication of the knocking condition in these tests. There seemed to be no timing retardation required during any steady-state speed part of the test cycle. For the whole cycle, the amount of throttle never exceeded 24%; normally, less than 10% was required. At an oxygen content of 25% the driver noticed little change in vehicle performance, except for smoother operation compared with normal-air (21% oxygen) operation.

Output from the knock sensor was fed to the vehicle's on-board computer to activate spark timing retardation. Evidently, the maximum allowable retardation in spark timing for this vehicle was not enough to alleviate the knocking problem when the oxygen content was higher than 28%. The knocking at high oxygen content was probably due to an increase in flame speed. This caused the burned mixture to expand rapidly; and when the gases compressed the unburned mixture, low-temperature chemical reactions (auto-ignition) resulted and led to a knocking condition. The fact that the mixture had the oxygen-enriched air could also have increased the knocking tendency. However, at an oxygen content of 25%, flame speed was not increased by much, and the unburned gas mixture would not have been compressed fast enough to initiate such an auto-ignition condition.

3.2 ENGINE-OUT EMISSIONS

All emissions data presented are the averages of three separate FTP emissions tests (cold, stabilized, and hot phases) under identical operating conditions and procedures.

Almost 200 hydrocarbons were identified in the engine-out emissions, but only the most significant species were selected for analysis here. To facilitate the discussion these species were grouped into aldehydes, olefins, aromatics, and paraffins.

Engine-out emission testing was done for the following emissions: carbon monoxide (CO), hydrocarbons, aldehydes, olefins, aromatic compounds, paraffin, ozone, and NO_x. Tests

were run at 21% oxygen (normal air) and at 25% and 28% oxygen enrichment for each of the three phases. Emissions were collected in bags as follows:

- Bag 1 (Cold Phase)
- Bag 2 (Stabilized Phase)
- Bag 3 (Hot Phase)

3.2.1 Carbon Monoxide Emission Testing

Carbon monoxide emissions were reduced by almost one-half at the cold phase of the FTP (bag one); there were few changes at the stabilized and hot phases (bags two and three) when the oxygen content of the air was 28%. These results and the weighted results are shown in Figure 3.1.

The reduction in CO emissions was caused mainly by the higher oxygen content and partially by the leaner-than-normal air combustion, as indicated by the higher oxygen concentration in the exhaust gas, especially during the first two to three minutes of the cold phase. (Note: the total cold phase runs for 505 seconds.) This leaner condition resulted from the inability of the vehicle's air/fuel management system to handle the high-oxygen-content air. Nevertheless, these results show that the engine was capable of burning leaner (around 10-20% less fuel), without misfiring, with the oxygen-enriched air.

FIGURE 3.1 Effects of Oxygen-Enriched Intake Air on Engine-Out CO Emissions

3.2.2 Hydrocarbon Emission Testing

Total FTP hydrocarbon emissions were reduced by one-half to two-thirds in all three bags at oxygen contents of 25 and 28%, respectively, as shown in Figure 3.2. Increasing the oxygen content from 25 to 28% yielded only minimal reductions.

3.2.3 Aldehyde Emission Testing

Aldehydes are important for ozone formation; they have an offensive smell in addition to their harmful health effects. Both formaldehyde and acetaldehyde emissions (1990 CAA toxic air pollutants) are extremely high with OH-containing fuels, such as methanol and ethanol, and C-O-C-containing species, such as ethers. The aldehyde emission problem is the major obstacle to the widespread use of alcohol fuels in spark-ignition engines. Even the most up-to-date catalytic converters have not solved this problem, according to the most recent data collected by the National Renewable Energy Laboratory (NREL).⁴

The use of oxygen-enriched air significantly decreased aldehyde emissions, as shown in Figure 3.3. The mechanisms for the reduction are not clear, but the results seem to indicate that the higher concentration of oxygen in the combustion chamber did not favor the formation of OH and C=O, even if more than enough hydrogen and oxygen were available. In the case of alcohols and ethers, the chemically-bonded oxygen atoms are in either C-OH or C-O-C bonds, which may well serve as the building blocks for the aldehydes containing both the C-OH and C=O bonds. Therefore, the oxygen-enrichment technique may be a better way to reduce carbon monoxide than oxygenated gasoline, which uses alcohols or ethers (such as MTBE and ETBE) to increase the oxygen content of gasoline.

FIGURE 3.2 Effects of Oxygen-Enriched Intake Air on Engine-Out Hydrocarbon Emissions

FIGURE 3.3 Effects of Oxygen-Enriched Intake Air on Engine-Out Aldehyde Emissions

When the oxygen content was increased from 25 to 28%, three out of four aldehydes showed slight increases in emissions. This significant trend was unique to the aldehydes. If aldehyde mechanisms are dictated by oxygen concentration, a further increase in oxygen concentration may have accelerated the formation reactions of the aldehydes. An analogy is the effects of oxygen in the formation and oxidation processes of particulates in combustion systems. Depending on the concentration of oxygen, oxygen can either be the particulates oxidizer or the catalyst for pyrolysis of hydrocarbons, leading to the formation of more particulates.⁵

3.2.4 Olefin Emission Testing

Olefins are also significant contributors to smog and ozone, particularly in the five species depicted in Figure 3.4. In general, substantial reductions were obtained with the 25%-oxygen-content air (compared with normal air combustion), but an additional 3% oxygen did not yield any additional reductions. The species 1,3-butadiene, which has two double bonds and is a CAA air toxic pollutant, had the highest level of reduction among the olefins, at close to 80% when compared with normal air. This is a reasonable result, because the most reactive combustion by-products are most likely to react with the available oxygen when there are fewer nitrogen molecules to inhibit reaction.

3.2.5 Aromatic Emission Testing

In addition to benzene (a carcinogen), which is identified as a CAA toxic air pollutant, there were other aromatics that existed in significant amounts in the engine-out emissions. Again, such compounds were reduced drastically with the 25%-oxygen-content air, compared with normal air. However, an additional 3% oxygen increase had very little improvement, as shown in Figure 3.5. One of the shortcomings of the hydrocarbon speciation technique is that compounds containing more than 12 carbons cannot be identified. Therefore, several polycyclic aromatic compounds remained unidentified.

The harmful health effects of many polycyclic compounds have been reported in various medical studies. Their allowable emission levels from any combustion system will certainly be legislated as soon as reliable techniques become available to identify and measure these compounds. The future for oxygen enrichment in reducing these aromatics in engine-out emissions is promising.

3.2.6 Paraffin Emission Testing

The last group of hydrocarbon compounds is the paraffins, which are extremely difficult to convert into less harmful hydrocarbons, carbon dioxide, and water at the catalytic converter. Here, oxygen enrichment reduced most of the paraffins by more than 50% at the

FIGURE 3.4 Effects of Oxygen-Enriched Intake Air on Engine-Out Olefin Emissions

FIGURE 3.5 Effects of Oxygen-Enriched Intake Air on Engine-Out Aromatic Emissions

25%-oxygen-content air, when compared with normal air. However, the reduction of methane was only about 20% (Figure 3.6) at the 25% oxygen level; at the 28% oxygen level, methane did not decrease significantly, primarily because methane is harder to break down than the other paraffins.

3.2.7 Ozone Emission Testing

The benefits of intake-air oxygen enrichment for the reduction of ozone had been investigated by means of the Carter maximum incremental reactivity (MIR) and the maximum ozone incremental reactivity (MOIR) factors.⁶ MIR represents an atmospheric condition that is low in hydrocarbons (HC) and has a low HC/NO_x ratio; ozone formation

FIGURE 3.6 Effects of Oxygen-Enriched Intake Air on Engine-Out Paraffin Emissions

is limited by the availability of hydrocarbons. MOIR similarly represents atmospheric conditions when (1) both hydrocarbons and NO_x are important, (2) the HC/NO_x ratio is moderate, and (3) the total ozone formation is at a maximum. Because of the lack of understanding of atmospheric chemistry, there are uncertainties in both factors, so that these ozone estimates must be interpreted carefully. Because oxygen enrichment had changed the composition of the hydrocarbons in the engine-out emissions, the integrated effects of these individual hydrocarbons on ozone needs to be analyzed.

With the 25%-oxygen-content air (Figure 3.8), there was an ozone reduction of approximately 50% in the three FTP bags and the weighted amount, when the MIR scale was used. Similarly, there was a 45% ozone reduction when the MOIR scale was used. With the 28%-oxygen-content air (Figure 3.8), the weighted ozone was only further reduced slightly, except in FTP bag 1 where the reduction was almost twice that of either bag 2 or bag 3.

3.2.8 NO_x Emission Testing

The results plotted in Figure 3.9 clearly show that NO_x emissions were all increased between three and five times in the three bags with the oxygen-enriched air. A solution to this problem of high NO_x emissions remains to be developed.

FIGURE 3.7 Effects of Oxygen-Enriched Intake Air on Engine-Out Ozone Emissions

FIGURE 3.8 Effects of Oxygen-Enriched Intake Air on Engine-Out Ozone Reductions

FIGURE 3.9 Effects of Oxygen-Enriched Intake Air on Engine-Out NO_x Emissions

3.2.9 Remarks

The drastic reductions in hydrocarbon species in engine emissions and their subsequent ozone reductions are the result of two major factors associated with oxygen enrichment. First, on a weight basis, there is less of a gas mixture because there is a slight decrease in volumetric efficiency and there is less nitrogen than the normal air; therefore, there are fewer nitrogen molecules to be heated before and during combustion. The gas temperature increases and accelerates all reactions. Second, by having fewer nitrogen molecules, radicals can react with the hydrocarbons more quickly because there will be fewer nitrogen molecules in the way. Reaction rates in general are directly proportional to fruitful collision frequency among atoms, radicals, and molecules. Unfortunately, these two factors are also conducive to the generation of NO_x , especially when the gas temperature is higher than that in normal air combustion.

3.3 CATALYTIC CONVERTER-OUT EMISSIONS

The results reported here are the averages of values obtained in three separate FTP emissions tests performed under the same operating conditions and procedures. Both the carbon monoxide and hydrocarbon emissions were substantially reduced by the oxygen enrichment of the intake air. These emissions levels were even lower than the year 2004 (Tier II) light-duty-vehicle emissions standards (1.7 g CO/mi and 0.125 g HC/mi), except for the NO_x emissions.

Again, there were almost 200 hydrocarbons identified in the catalytic converter-out emissions, and only four groups of species (aldehyde, olefins, aromatic, and paraffins) that are significant to air pollution were selected for analysis.

Catalytic converter-out emission testing was done for the following emissions: carbon monoxide (CO), hydrocarbon, aldehyde, olefin, aromatic, paraffin, ozone, and NO_x . Tests were made at 21% oxygen (normal air) and at 25 and 28% oxygen enrichment for each of the three phases. Emissions were collected in bags as follows:

- Bag 1 (Cold Phase)
- Bag 2 (Stabilized Phase)
- Bag 3 (Hot Phase)

3.3.1 Carbon Monoxide Emission Testing

The catalytic converter had shown a significant increase in carbon monoxide conversion efficiency with oxygen enrichment, compared with vehicle operation with normal air (Figure 3.10). The greatest improvement (lower CO) was in the cold phase of the FTP (bag 1), during which the engine was running with the 25 and 28% oxygen air. Apparently,

FIGURE 3.10 Effects of Oxygen-Enriched Intake Air on Catalytic Converter-Out CO Emissions

the additional oxygen in the converter simply provided more oxygen for the catalytic oxidation of the carbon monoxide, and the higher oxygen content also promoted the conversion reactions in the cold phase. In addition, there were substantially fewer hydrocarbons to compete with carbon monoxide for oxygen. There was no temperature increase in the engine exhaust with oxygen enrichment. However, the improvement (lower CO) in the hot phase (bag 3) was due neither to the additional oxygen nor to the higher exhaust temperature, as indicated by the data on oxygen concentration and temperature of the gases entering the converter.

Two other major differences with oxygen enrichment were as follows: (1) much lower levels of hydrocarbons and (2) much higher NO_x levels coming into the catalytic converter. These two differences could, collectively or singularly, affect the carbon monoxide oxidation process. The exhaust-gas temperature at the converter was less than 1000°F , well below the temperature (1600°F) necessary for any significant water/gas reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$). The importance of this finding is that these data seem to confirm the current theory in catalysis that hydrocarbons play a very complex role in both the catalytic carbon monoxide oxidation and NO_x conversion processes.

3.3.2 Hydrocarbon Emission Testing

The total catalytic converter-out FTP hydrocarbons, as measured by a flame ionization detector (FID), showed drastic reductions in all three bags, again with oxygen enrichment (Figure 3.11). These improvements came mainly from the engine, not from the converter. By using both the engine-out and converter-out emissions data, the total

FIGURE 3.11 Effects of Oxygen-Enriched Intake Air on Catalytic Converter-Out Hydrocarbon Emissions

hydrocarbon conversion efficiencies were calculated for the converter. At the 25 and 28% oxygen levels, there was a slight decrease in conversion efficiency in both the cold and the stabilized phases and a marginal increase in the hot phase, when compared with the 21% oxygen (normal air). These small differences probably reflect experimental uncertainties.

3.3.3 Aldehyde Emission Testing

The converter-out aldehydes, as shown in Figure 3.12, were mostly from the cold phase, and the weighted emissions were less than 5 mg/mi at all oxygen levels. In comparing the aldehyde emissions of the engine-out with those of the converter-out, there was a drastic decrease in the cold-phase aldehyde-conversion efficiency when the 25%-oxygen-content air was used instead of normal air (21% oxygen). The average conversion efficiency for the four aldehydes dropped from 85% at normal air to 54% at 25%-oxygen-content air. This efficiency returned to 85% when 28%-oxygen-content air was used. This peculiarity points out the sensitivity of aldehyde reactions to a slightly different oxygen concentration in the system. In the first two to three minutes of FTP cold-phase operation with oxygen-enriched air, there was more oxygen in the converter than in the normal air operation, but this did not hold true for the rest of the test cycle. Further understanding of aldehyde oxidation chemistry is needed for converter development.

FIGURE 3.12 Effects of Oxygen-Enriched Intake Air on Catalytic Converter-Out Aldehyde Emissions

3.3.4 Olefin Emission Testing

The catalytic converter-out reactive olefins were only significant in the cold phase of the FTP, as shown in Figure 3.13. The weighted emissions were all less than 15 mg/mi, and they were approximately halved with the 25%-oxygen-content air, as compared with normal air. An additional 3% oxygen in intake air had very little effect on reducing the emissions. In the cold phase, there was a trend toward increasing conversion efficiency with increasing oxygen content on the basis of the average conversion efficiencies of the five olefins. However, the improvement amounted to only a few percent. 1,3-Butadiene showed the most reduction, from about 1 mg/mi at normal air to 0.08 mg/mi at 28%-oxygen-content air.

3.3.5 Aromatic Emission Testing

The catalytic converter-out aromatics were most prominent in the cold phase of the FTP, as shown in Figure 3.14. The converter significantly reduced the levels of aromatics, while oxygen enrichment decreased the levels of weighted aromatics to the few-milligram-per-mile range in the standard and hot phases. Conversion efficiency improved slightly with the 25%-oxygen-content air compared with normal air, but that improvement disappeared when oxygen content was increased to 28%.

3.3.6 Paraffin Emission Testing

The paraffins were the most difficult to convert into other species and had the lowest conversion efficiencies of the four hydrocarbon groups discussed here. In general, the cold phase had the highest catalytic converter-out emissions of the three phases (Figure 3.15). The catalytic converter-out methane had the lowest level of reduction in comparison with the other paraffins, because of the low reduction in the engine and the modest converter efficiency in the cold phase with oxygen enrichment. This behavior of the converter with oxygen enrichment is similar to that in the engine, discussed earlier (Sub-section 3.2.6).

3.3.7 Ozone Emission Testing

In terms of the Carter MIR and MOIR factors, the 25%-oxygen-content air reduced the FTP weighted ozone by about 60%, while the 28%-oxygen-content air yielded no further significant reductions (Figure 3.16). In the stabilized and hot-phases there were significant ozone reductions of between 12-23% when the oxygen content of the intake air was increased from 25 to 28% (Figure 3.17). This result was just the opposite of that for the engine-out emissions (sub-section 3.2.7), which had the best ozone reduction in the cold phase (compared with the other two phases) when the oxygen content was increased by 3% from the 25%-oxygen-content air. Further studies are needed to explain this significant trend.

FIGURE 3.13 Effects of Oxygen-Enriched Intake Air on Catalytic Converter-Out Olefin Emissions

FIGURE 3.14 Effects of Oxygen-Enriched Intake Air on Catalytic Converter-Out Aromatic Emissions

3.3.8 NO_x Emission Testing

The increase in NO_x emissions (Figure 3.18) as a result of oxygen enrichment of the intake air was significant. To bring the NO_x emissions to the year 2004 (Tier II) standard of 0.2 g/mi, a catalytic converter efficiency in excess of 95% would be required for this vehicle. The catalytic converter had also shown a significant decrease in NO_x conversion efficiency as a result of oxygen enrichment of the intake air. The decrease was from 75% efficiency with normal air to about 39% efficiency with oxygen-enriched air. This degradation might be due to the oxidizing environment, the lower hydrocarbon concentration, and the order-of-magnitude increase in NO_x concentration because the catalytic converter was not designed to handle these very different conditions.

FIGURE 3.15 Effects of Oxygen-Enriched Intake Air on Catalytic Converter-Out Paraffin Emissions

FIGURE 3.16 Effects of Oxygen-Enriched Intake Air on Catalytic Converter-Out Ozone Emissions

3.3.9 Remarks

The performance and emissions characteristics of the engine and the catalytic converter apparently did not measurably change after the series of oxygen enrichment experiments. However, these tests were brief, and the results reported here should not be extrapolated to predict the long-term effects of oxygen enrichment on the engine and on the catalytic converter.

3.4 EMISSION CALCULATIONS USING OXYGEN ENRICHMENT RESULTS ON 1991 VEHICLES

An assessment was also conducted by using the oxygen-enrichment results to determine whether the NO_x emission problem could be overcome. The supposition was that if the vehicle had a low- NO_x -emission engine, but hydrocarbon and carbon monoxide emissions were relatively higher, this oxygen-enrichment technique would decrease the emissions of hydrocarbons and carbon monoxide and the emissions of NO_x would increase, but the vehicle could still meet all the 2004 Tier II standards.

FIGURE 3.17 Effects of Oxygen-Enriched Intake Air on Catalytic Converter-Out Ozone Reductions

FIGURE 3.18 Effects of Oxygen-Enriched Intake Air on Catalytic Converter-Out NO_x Emissions

Light-duty-vehicle certification results⁷ were reviewed for the 1991 model year, and five vehicle models (Baretta, Capri, Le Baron, Corolla, and Cabriolet) were found to produce extremely low NO_x emissions. By using the three-way catalytic-converter conversion efficiencies for the carbon monoxide, hydrocarbon, and NO_x emissions (of the 1990 Lumina running under ambient air conditions), the investigators back-calculated the engine emissions of these 1991 vehicles using normal air. It was assumed that the 1991 vehicles would behave the same way as the 1990 Lumina at 25%-oxygen-content air. The engine-out NO_x, hydrocarbon, and carbon monoxide emissions were calculated by using the 1990 Lumina engine data (i.e., at 25%-oxygen-content air, hydrocarbons, were reduced by 51%, carbon monoxide was reduced by 2%, and NO_x was increased by 377%). These calculations showed the engine emissions would pass through the 1991 catalytic converter with 90% reduction efficiencies for carbon monoxide and hydrocarbons and an 80% reduction efficiency for NO_x. The simulated, FTP-weighted emissions are shown in Figure 3.19.

Both hydrocarbon and carbon monoxide emissions were below the year 2004 Tier II standards for all five vehicles, and three vehicles had NO_x emissions lower than the standard. This simple extrapolation showed that NO_x emissions would be a problem in most vehicles, but the problem would be surmountable, provided that the catalytic converter could perform more efficiently under an oxidizing environment. The recently developed catalytic converters for lean-burn engines (spark ignition) can certainly benefit the oxygen-enrichment technology.

25% oxygen, nitrogen oxides conversion efficiency of 80%

FIGURE 3.19 Potential of Oxygen-Enriched Intake Air to Meet 2004 Standards

4 CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

On the basis of the results of this experiment, it is clear that even with a production vehicle, oxygen enrichment yields benefits. These benefits were the reductions in carbon monoxide and hydrocarbon emissions from the engine and from the catalytic converter, especially during the cold phase of the FTP emissions test. This technique could be an alternative to the heated catalytic converter. The tests showed that oxygen-enriched air reduced the levels of hydrocarbons and carbon monoxide in the engine chamber. The tests also established that the higher oxygen content in the exhaust, not the higher exhaust temperature, accelerated the catalytic reactions leading to substantial reductions in carbon monoxide emissions in the cold phase. In addition, fewer hydrocarbons were present to compete with the carbon monoxide for the oxygen in the catalytic converter.

The hydrocarbon speciation results clearly indicate that reactive species (such as 1,3 butadiene) were remarkably reduced, both in the engine and in the catalytic converter, with the oxygen-enriched air. Similarly, both formaldehyde and acetaldehyde were reduced drastically in the engine, while modest reductions were made in the catalytic converter. The 60% reduction in ozone emissions with the 25%-oxygen-content air (compared with normal air) is another significant benefit of this technology.

The significant increase in engine-out NO_x emissions (in all phases of the FTP emissions test) was expected, because the oxygen-enriched air increased the flame speed, and combustion progressed rapidly to produce extremely hot gases. Even though these gases had more time (because of a shorter combustion duration) to cool down during the engine expansion stroke, cooling was not rapid enough to quench the gases and prevent additional NO_x formation. The increase in the catalytic converter-out NO_x was exacerbated by reduced converter efficiency under the oxidizing environment and by the extremely high NO_x concentration in the exhaust gas.

4.2 RECOMMENDATIONS

The most significant reductions in both hydrocarbons and carbon monoxide due to oxygen enrichment were observed at the beginning of the cold phase of the FTP emissions test; these observations should be given serious consideration. In this experiment, no modifications were made to the oxygen-sensing or the fuel-management systems; thus, the engine must have been running leaner than necessary in the first two to three minutes because of the inadequate response of the system to the oxygen-enriched air in the cold phase. Obviously, the engine itself could be re-optimized for oxygen-enriched-air operation; for example, the timing retardation limit could be extended. Another possible design change would be to lower the engine compression ratio to reduce the knocking sensitivity.

If the algorithm and oxygen sensor of the air/fuel-management systems were modified to accommodate the excess oxygen, the NO_x emissions would be reduced in the beginning of the cold phase, while carbon monoxide emissions would also be reduced. It is also recommended that the instantaneous emissions of carbon monoxide, hydrocarbons, and NO_x (both from the engine and from the catalytic converter) be measured to find out their real-time characteristics. Hydrocarbon speciation for the first two to three minutes of the cold-phase emissions would also reveal which hydrocarbons are emitted and abolished in the catalytic converter.

The results of this experiment suggest that the engine is more tolerant of a lean-burn operation (lack of misfiring problems) with oxygen enrichment. Thus, the oxygen-enriched air may improve the combustion stability of current lean-burn engines. Oxygen enrichment also has the potential of further increasing the lean-burn limit of such engines (perhaps as high as 30:1) without causing misfiring and other problems. It is highly recommended that oxygen-enrichment experiments be carried out on a lean-burn engine.

On the basis of the emissions results, it is estimated that several low- NO_x -emission vehicles (presently in service) could meet the year 2004 (Tier II) emissions standards if they used 25%-oxygen-content air and were equipped with catalytic converters with 80% conversion efficiency for NO_x . Such a bench-mark experiment should be done to demonstrate that oxygen enrichment is a viable way to reduce emissions from older vehicles, allowing them to meet future emissions standards. Further studies should then concentrate on economic assessment of an oxygen-enrichment system.

With respect to methanol and ethanol, one of the potential benefits may be slightly improved fuel efficiency. Because of the excellent anti-knocking quality of these alternative fuels, the timing does not have to be retarded as much as for gasoline-fueled operation. Oxygen-enriched air will probably reduce aldehyde emissions; the extent of the reduction merits investigation. Experiments with oxygenated gasoline (with a known oxygen content) should be run so that results can be compared with the oxygen-enriched-air results (with an equal amount of oxygen). Experimental results would then show if use of oxygen enrichment or oxygenated gasoline would be a better way to reduce carbon monoxide, hydrocarbon, and aldehyde emissions. Experiments with gasoline containing a high aromatic content should also be run with oxygen-enriched air to determine if smoother combustion, with fewer pollutants, could be achieved.

A prototype oxygen-enrichment system (using a polymeric membrane) can be retrofitted into a conventional vehicle to show that such a system is feasible and that tangible emission benefits result. Even though a retrofit membrane oxygen-enrichment system might be bulky and not optimized, a successful vehicle demonstration would certainly position the technique as a viable emission abatement scheme. Upon completion of a successful vehicle demonstration, this system could then be recommended to the automotive and oil industries and to the various government pollution control agencies. A prototype vehicle system demonstration would pave the way for commercialization of the oxygen-enrichment technology in the future.

5 REFERENCES

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APPENDIX:
EQUIPMENT AND DATA

APPENDIX:

EQUIPMENT AND DATA

A.1 EQUIPMENT PHOTOGRAPHS

Figure A.1 Total Oxygen Enrichment System.

Figure A.2 Oxygen Air Mixing Chamber.

A.2 DATA

The large volume of data collected for this experiment cannot be reproduced here in detail. The emission data for carbon monoxide, hydrocarbons, oxides of nitrogen, and carbon dioxide are included here. In addition, the hydrocarbon speciation data for methane, benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and methanol are included. All the data have been recorded both on paper and on 3.5-in. microdisk.

Tables A.2.1 through A.2.8 give additional experimental data.

FIGURE A.1 Total Oxygen Enrichment System

FIGURE A.2 Oxygen Air Mixing Chamber

TABLE A.2.1 Engine-Out Emissions

Test Date	090192	090292	090992	091092	091192	100192	090392	090492	100692
Test Number	2572	2575	2580	2582	2585	2610	2576	2578	2615
Intake Air O2 (%)	21	21	21	25	25	25	28	28	28
Type	Engine Out								
Bag 1 (gm/mile)									
HC	2.91	3.46	2.92	1.64	1.43	1.52	1.06	1.16	1.13
CO	17.75	18.18	18.80	13.09	12.63	13.11	9.55	9.96	10.87
NO _x	2.87	2.88	3.11	9.98	9.89	9.93	11.90	13.05	14.42
CO ₂	444.96	440.58	444.42	462.70	437.53	465.63	469.09	495.20	567.96
MPG	18.4	18.4	18.3	18.1	19.1	18.0	18.1	17.2	15.0
Bag 2 (gm/mile)									
HC	2.74	2.93	2.74	1.32	1.32	1.41	1.03	1.08	1.07
CO	15.26	15.03	13.77	17.49	15.30	16.15	15.11	15.35	15.00
NO _x	1.78	1.62	1.79	7.61	7.46	7.70	10.58	10.75	11.50
CO ₂	447.89	441.79	450.10	493.60	441.07	461.99	489.20	490.72	512.23
MPG	18.4	18.6	18.4	16.8	18.8	18.0	17.1	17.1	16.4
Bag 3 (gm/mile)									
HC	2.14	2.14	2.16	1.05	1.05	1.11	0.86	0.85	0.82
CO	12.25	10.78	11.48	11.25	11.14	11.25	10.07	12.20	10.33
NO _x	2.58	2.36	2.74	8.36	8.66	8.55	11.18	11.46	11.65
CO ₂	378.16	344.34	381.23	386.02	389.03	398.61	420.80	440.32	444.52
MPG	21.9	24.0	21.8	21.7	21.6	21.0	20.1	19.1	19.1
Weighted Ave. (gm/mile)									
HC	2.61	2.83	2.61	1.31	1.27	1.35	0.99	1.03	1.01
CO	14.95	14.52	14.18	14.87	13.61	14.18	12.57	13.37	12.86
NO _x	2.23	2.08	2.32	8.31	8.29	8.40	11.02	11.42	12.15
CO ₂	428.10	414.98	429.83	457.67	426.05	445.41	466.24	477.83	505.15
MPG	19.3	19.8	19.2	18.2	19.6	18.7	18.1	17.6	16.7

TABLE A.2.2 Averaged Engine-Out Emissions

	21% Oxygen	25% Oxygen	28% Oxygen
Bag 1 (gm/mile)			
HC	3.10	1.53	1.12
CO	18.24	12.94	10.13
NO _x	2.95	9.93	13.12
CO ₂	443.32	455.29	510.75
MPG	18.4	18.4	16.8
Bag 2 (gm/mile)			
HC	2.80	1.35	1.06
CO	14.69	16.31	15.15
NO _x	1.73	7.59	10.94
CO ₂	446.59	465.55	497.38
MPG	18.5	17.9	16.9
Bag 3 (gm/mile)			
HC	2.15	1.07	0.84
CO	11.50	11.21	10.87
NO _x	2.56	8.52	11.43
CO ₂	367.91	391.22	435.21
MPG	22.6	21.4	19.4
Weighted Ave. (gm/mile)			
HC	2.68	1.31	1.01
CO	14.55	14.22	12.93
NO _x	2.21	8.33	11.53
CO ₂	424.30	443.04	483.07
MPG	19.4	18.8	17.5

TABLE A.2.3 Catalytic Converter-Out Emissions

Test Date	091592	091692	092492	091892	092192	092592	092292	092392	092992
Test Number	2588	2593	2600	2594	2596	2602	2597	2599	2606
Intake Air O2 (%)	21	21	21	25	25	25	28	28	28
Type	Converter Out								
Bag 1 (gm/mile)									
HC	0.76	0.86	1.01	0.39	0.78	0.40	0.37	0.32	0.43
CO	6.08	8.93	13.46	2.11	5.68	2.20	2.33	1.67	1.54
NO _x	1.19	1.04	0.96	6.43	5.91	6.18	9.71	11.61	11.06
CO ₂	455.08	467.39	466.57	482.34	478.36	492.54	508.08	533.96	514.24
MPG	18.9	18.3	18.0	18.2	18.0	17.8	17.2	16.4	17.1
Bag 2 (gm/mile)									
HC	0.09	0.09	0.08	0.06	0.05	0.04	0.02	0.05	0.05
CO	1.32	1.67	1.21	2.03	1.09	1.21	0.54	1.14	1.15
NO _x	0.33	0.31	0.37	2.46	2.96	2.74	5.40	5.68	5.15
CO ₂	476.36	482.92	474.37	488.63	480.99	485.54	510.84	527.74	514.58
MPG	18.5	18.2	18.5	18.0	18.3	18.1	17.3	16.7	17.1
Bag 3 (gm/mile)									
HC	0.24	0.13	0.16	0.06	0.07	0.06	0.04	0.04	0.04
CO	3.73	1.60	1.43	1.24	1.09	0.89	0.44	0.77	1.00
NO _x	0.51	0.54	0.55	3.64	3.80	3.56	6.29	7.62	6.00
CO ₂	393.03	413.27	399.36	425.32	419.94	418.84	450.74	453.89	439.57
MPG	22.1	21.2	22.0	20.7	20.9	21.0	19.6	19.4	20.0
Weighted Ave. (gm/mile)									
HC	0.27	0.26	0.30	0.13	0.21	0.12	0.10	0.10	0.13
CO	2.97	3.15	3.83	1.83	2.04	1.32	0.88	1.15	1.19
NO _x	0.56	0.52	0.54	3.60	3.80	3.67	6.54	7.44	6.61
CO ₂	449.05	460.62	452.06	470.17	463.68	468.64	493.74	508.70	493.92
MPG	19.4	18.9	19.3	18.7	18.9	18.8	17.8	17.3	17.8

TABLE A.2.4 Averaged Catalytic Converter-Out Emissions

	21% Oxygen	25% Oxygen	28% Oxygen
Bag 1 (mg/mile)			
HC	0.88	0.52	0.37
CO	9.49	3.33	1.85
NO _x	1.06	6.17	10.79
CO ₂	463.01	484.41	518.76
MPG	18.4	18.0	16.9
Bag 2 (mg/mile)			
HC	0.09	0.05	0.04
CO	1.40	1.44	0.94
NO _x	0.34	2.72	5.41
CO ₂	477.88	485.05	517.72
MPG	18.4	18.1	17.0
Bag 3 (mg/mile)			
HC	0.18	0.06	0.04
CO	2.25	1.07	0.74
NO _x	0.53	3.67	6.64
CO ₂	401.89	421.37	448.07
MPG	21.8	20.9	19.7
Weighted Ave. (mg/mile)			
HC	0.28	0.15	0.11
CO	3.32	1.73	1.07
NO _x	0.54	3.69	6.86
CO ₂	453.91	467.50	498.79
MPG	19.2	18.8	17.6

TABLE A.2.5 Selected Engine-Out Hydrocarbon Emissions

Test Date	090192	090292	090992	091092	091192	100192	090392	090492	100692
Test Number	2572	2575	2580	2582	2585	2610	2576	2578	2615
Intake Air O2 (%)	21	21	21	25	25	25	28	28	28
Type	Engine Out								
Bag 1 (mg/mile)									
Methane	NA	114	100	72	60	NA	52	68	NA
Benzene	NA	144	126	79	80	NA	54	51	NA
1,3-Butadiene	NA	33	9	7	2	NA	3	6	NA
Formaldehyde	NA	110	113	36	49	NA	80	26	NA
Acetaldehyde	NA	28	23	5	11	NA	14	2	NA
Methanol	NA	15	17	9	11	NA	10	10	NA
Bag 2 (mg/mile)									
Methane	NA	86	86	63	71	NA	59	61	NA
Benzene	NA	100	132	60	69	NA	64	61	NA
1,3-Butadiene	NA	33	6	6	0	NA	3	4	NA
Formaldehyde	NA	96	116	70	65	NA	28	78	NA
Acetaldehyde	NA	24	22	15	16	NA	4	14	NA
Methanol	NA	16	12	9	9	NA	4	7	NA
Bag 3 (mg/mile)									
Methane	NA	65	67	53	52	NA	43	46	NA
Benzene	NA	70	85	46	46	NA	46	46	NA
1,3-Butadiene	NA	20	7	6	2	NA	3	4	NA
Formaldehyde	NA	93	103	47	50	NA	52	50	NA
Acetaldehyde	NA	19	19	10	12	NA	10	10	NA
Methanol	NA	8	13	6	12	NA	8	13	NA
Weighted Ave. (mg/mile)									
Methane	NA	86	84	62	64	NA	53	58	NA
Benzene	NA	101	118	60	65	NA	57	55	NA
1,3-Butadiene	NA	30	7	6	1	NA	3	5	NA
Formaldehyde	NA	98	112	56	58	NA	45	60	NA
Acetaldehyde	NA	24	22	12	14	NA	8	10	NA
Methanol	NA	14	13	8	11	NA	6	9	NA

TABLE A.2.6 Averaged Engine-Out Hydrocarbon Emissions

	21% Oxygen	25% Oxygen	28% Oxygen
Bag 1 (mg/mile)			
Methane	107	66	60
Benzene	135	80	53
1,3-Butadiene	21	5	5
Formaldehyde	112	43	53
Acetaldehyde	26	8	8
Methanol	16	10	10
Bag 2 (mg/mile)			
Methane	86	67	60
Benzene	116	65	63
1,3-Butadiene	20	3	4
Formaldehyde	106	68	53
Acetaldehyde	23	16	9
Methanol	14	9	6
Bag 3 (mg/mile)			
Methane	66	53	45
Benzene	78	46	46
1,3-Butadiene	14	4	4
Formaldehyde	98	49	51
Acetaldehyde	19	11	10
Methanol	11	9	11
Weighted Ave. (mg/mile)			
Methane	85	63	56
Benzene	110	63	56
1,3-Butadiene	19	4	4
Formaldehyde	105	57	53
Acetaldehyde	23	13	9
Methanol	14	10	8

TABLE A.2.7 Selected Catalytic Converter-Out Hydrocarbon Emissions

Test Date	091592	091692	092492	091892	092192	092592	092292	092392	092992
Test Number	2588	2593	2600	2594	2596	2602	2597	2599	2606
Intake Air O2 (%)	21	21	21	25	25	25	28	28	28
Type	Converter Out								
Bag 1 (mg/mile)									
Methane	67	79	86	33	75	37	32	33	42
Benzene	36	42	38	14	37	16	16	15	20
1,3-Butadiene	7	0	5	1	3	2	0	0	0
Formaldehyde	18	18	10	11	14	20	4	7	12
Acetaldehyde	5	5	4	2	4	4	0	0	0
Methanol	3	5	NA	5	2	1	3	NA	NA
Bag 2 (mg/mile)									
Methane	48	45	30	46	35	33	12	35	28
Benzene	4	4	3	1	1	1	1	1	1
1,3-Butadiene	0	0	0	0	0	0	0	0	0
Formaldehyde	3	3	1	1	2	0	0	1	9
Acetaldehyde	0	0	1	0	0	0	0	0	0
Methanol	0	0	NA	1	1	0	0	NA	NA
Bag 3 (mg/mile)									
Methane	52	39	33	30	33	26	21	25	25
Benzene	13	4	8	1	2	3	2	2	1
1,3-Butadiene	2	0	0	0	0	0	0	0	0
Formaldehyde	1	2	0	0	0	7	0	2	7
Acetaldehyde	0	0	1	0	0	0	0	0	0
Methanol	4	0	NA	3	2	0	2	NA	NA
Weighted Ave. (mg/mile)									
Methane	53	50	42	39	43	32	19	31	30
Benzene	13	12	12	4	9	4	4	4	5
1,3-Butadiene	2	0	1	0	1	0	0	0	0
Formaldehyde	6	6	3	3	4	6	1	2	9
Acetaldehyde	1	1	1	1	1	1	0	0	0
Methanol	2	1	NA	2	1	0	1	NA	NA

**TABLE A.2.8 Averaged Catalytic Converter-Out
Hydrocarbon Emissions**

	21% Oxygen	25% Oxygen	28% Oxygen
Bag 1 (mg/mile)			
Methane	77	48	36
Benzene	39	22	17
1,3-Butadiene	4	2	0
Formaldehyde	15	15	8
Acetaldehyde	5	3	0
Methanol	4	3	3
Bag 2 (mg/mile)			
Methane	41	38	25
Benzene	4	1	1
1,3-Butadiene	0	0	0
Formaldehyde	2	1	3
Acetaldehyde	0	0	0
Methanol	0	1	0
Bag 3 (mg/mile)			
Methane	41	30	24
Benzene	8	2	2
1,3-Butadiene	1	0	0
Formaldehyde	1	2	3
Acetaldehyde	0	0	0
Methanol	2	2	2
Weighted Ave. (mg/mile)			
Methane	48	38	27
Benzene	12	6	4
1,3-Butadiene	1	0	0
Formaldehyde	5	4	4
Acetaldehyde	1	1	0
Methanol	2	1	1

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