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Aldehyde and BTX Emissions from a Light Duty Vehicle Fueled on Gasoline and Ethanol-Gasoline Blend, Operating with a Three-Way Catalytic Converter

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Abstract:

The current work is aimed at the experimental investigation of the aldehyde and BTX (benzene, toluene and Xylene) pollutants emitted from a light duty spark ignition (SI) vehicle fueled on gasoline and ethanol-gasoline blended fuel, operating with a three-way catalytic converter (TWC). At the same time, the specific reactivity (SR) of these pollutants has also been addressed in this paper. The experiments were performed on both transient as well as steady modes following the standard protocols recommended for light duty vehicles. Aldehyde and BTX species were analyzed using high performance liquid chromatography (HPLC) and gas chromatography/mass spectroscopy (GC/MS), respectively. During the transient cycle of operation, formaldehyde and BTX emissions were decreased, while acetaldehyde and acrolein+acetone pollutants were increased with (10% ethanol – 90% gasoline by volume), compared with E-0 (neat gasoline). During the steady modes, formaldehydes with E-0 were dominant to those with E-10 fuel. Acetaldehydes with E-10 showed dominancy to those with E-0, and were the most abundant components among the other aldehyde species. Formaldehydes were decreased with the increase in speed, and toluene was found to be the most abundant component of the BTX emissions with both the fuels. The BTX components displayed their maxima at lower speed mode and minima at medium speed mode for both the fuels, and were decreased in case of E-10, compared with E-0. The SR of the transient mode pollutants was lower as compared to that taken from the mean of the steady mode pollutants. In case of E-10, the SR of the pollutants was higher at both transient as well as steady modes, compare with E-0 fuel.

Keywords: Ethanol; Non-Regulated Emissions; Carbonyls; Three Way Catalytic Converter; Volatile Organic Compounds.

1. Introduction

The modern era of science and technology has changed the life style of human beings by facilitating them with increased fleet of buses, trucks, motor cars, aircrafts, ships, and agricultural and construction machinery. Consequently, the world has been forced to confront with the number of issues such as the energy crisis, global warming and environmental pollution leading to the harmful effects on human life. In order to meet the increasing energy needs, researchers are converging their attention to the alternative fuels like methanol, ethanol, liquefied petroleum gas (LPG), liquefied natural gas (LNG), compressed natural gas (CNG), vegetable oils and biodiesel.

Motor vehicle emissions are one of the major anthropogenic sources of air pollution and contribute to the deterioration of urban air quality [1]. When a new fuel is introduced in the market, a prerequisite is that pollutants emitted from a vehicle are not more toxic than those emanated when it is running on the standard market fuel [2]. Ethanol is an oxygenated, biodegradable, regenerative and promising alternative biofuel for vehicle engines with least adverse impacts on public health and environment. Carbon dioxide (CO_2) released by the burned ethanol can be fixed by growing plants and therefore makes less net greenhouse gas contribution to global warming, compared with fossil petroleum [3]. Ethanol is made up of a group of chemical compounds whose molecules contain a hydroxyl group (– OH) bounded to a carbon atom. So, its oxygen content favors the further combustion of gasoline blended with it [4].

Ethanol is considered to be an excellent fuel for spark ignition (SI) engines, having a high octane number and can be used without major engine modifications [2]. Its blend with gasoline has widely been used in many countries like USA, the European Union, Canada, Brazil and Thailand [5]. In China, the gasoline is being sold with an addition of 10% (v/v) ethanol in its nine provinces, with a primary motive to minimize the dependence on imported petroleum sources and to reduce the carbon monoxide

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(CO) and particulate matter (PM) [6]. Since 2001, all gasoline sold in eastern Sweden contains approximately 5% ethanol [2].

In the current study, E-10 (a mixture known as gasohol) has been used as an alternative fuel to E-0 in a gasoline car. Although some studies have been reported on regulated emissions from ethanol-gasoline blended fuels, unregulated emissions still need to be addressed comprehensively particularly, when the vehicle is equipped with a TWC. This study is focused on the comparative analysis of aldehydes and BTX emissions from a spark ignition vehicle fuelled with gasoline and its blend with ethanol, operating with a TWC system both on transient as well as steady modes. Furthermore, the ozone forming potential of the pollutants has also been discussed in terms of their SR. So, this study would be helpful to investigate the emissions of compound playing a critical role on tropospheric chemistry, and are considered to be toxic, mutagenic, and even carcinogenic to humans

2. Material and Methods

2.1. Test Vehicle, Fuels and Experimental Conditions

The experiments were performed on a 4 cylinder, 1.3-liter displacement volume, 60 kW, multi port fuel injected (PFI), dual fuelled, recent model EURO – III compliant vehicle equipped with a TWC designed and developed for minimum optimized regulated pollutants with E-10 fuel. The test vehicle was run on a 1.0 m single roll DC electrical chassis dynamometer (ONO SOKKI Inc.), according to cycle shown in Figure 1. Part one of this cycle consists of four sub-cycles which simulate the urban regions; while the part two of the cycle simulates the main motor-way/highway out of the urban regions. The average speed of the vehicle during the test was 33.58 km/h. In order to investigate the pollutants in the steady mode, the vehicle was run at the speeds of 40, 80 and 120 km/h for 300 seconds. In order to avoid the possible interference caused by the residues in oil pipeline, a separate fuel tank was used in this study. The schematic diagram of the experimental setup is given in Figure 2.

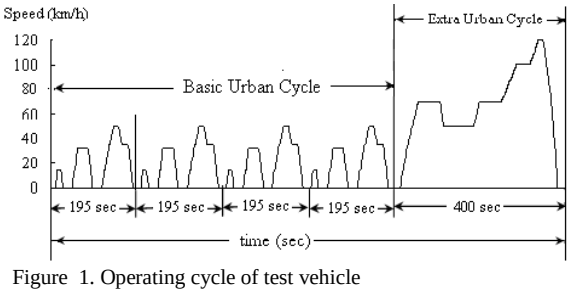


Figure 1. Operating cycle of test vehicle

The fuels used in this study are unleaded gasoline having research octane number (RON) 93 and gasoline-ethanol mixture containing 10% ethanol and 90% gasoline (v/v), with gasoline as a reference or baseline fuel. The properties of the fuels are listed in Table 1.

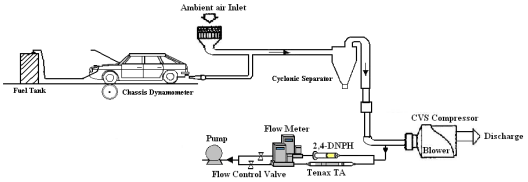


Figure 2. Experimental setup.

Table 1. Properties of the test fuels

Properties	Gasoline-ethanol blend	Gasoline
Density (Kg/L) at 20˚C	0.74	0.73
Gross heat content (MJ/kg)	42.2	46.0
Octane number	95.0	93.0
Oxygen content (wt %)	3.5	n/a
Carbonate content (wt %)	83.4	86.4
Hydrogen content (wt %)	13.1	13.6

2.2. Sampling Methodology

The sampling scheme is shown in Figure 1. In order to get a constant exhaust volume, a constant volume sampling (CVS) method consisting of a dilution tunnel of a standard critical flow venture was used. The exhaust from the vehicle was mixed with the fresh, filtered and low humidity atmospheric air to avoid the water condensation in the dilution tunnel. The atmospheric temperature and pressure were approximately 25°C and 100 kpa, respectively. The exhaust flow rate and the dilution ratio were 10 m^3/min and 15, respectively. The exhaust samples were taken in 2, 4-dinitrophenylhydrazine (DNPH) coated silica gel cartridges (Accustandard ® Inc.) and Tenax TA® tubes (Markes USA) for the aldehydes and BTX emissions, respectively. The DNPH inside the cartridges trapped the carbonyls to react with them and to form the corresponding stable 2, 4-dinitrophenylhydrazone derivatives. The sampling pumps were constant volume pumps (SKC USA, AirChek2000) and the sampling volume was 220 mL and it took 10 minutes to sample at every mode. Three samples of each E-0 and E-10 fuel were taken for the aldehyde and BTX species analyses. After sampling, the tubes were sealed with aluminum foil and were refrigerated at -10˚C.

2.3. Sample Extraction and Analysis

For the extraction of aldehydes trapped sample material, solid phase extraction (SPE) method was used, and the environment protection agency (EPA) standard method TO-11A [7] was used to analyze the aldehydes using HPLC (USA Agilent 1200LC) system with an automatic injector and an ultraviolet (UV) detector as discussed in detail elsewhere [8] .

In order to extract the species on Tenax TA®, automatic thermal desorber (TD), UNITY (Markes USA) was used in which Tenax tubes were first blown by the dry inert

gases and then heated, and the EPA standard method TO-17 [9]

was used for the qualitative and quantitative analyses of the BTX emissions using GC/MS as discussed in detail elsewhere [10] however, Table 2 is given to show the scheme of thermal desorber, gas chromatograph and mass spectrometer (TD-GC/MS) system.

Table 2 .TD- GC/MS specifications [10]

Thermal desorber (TD)	Tube: 280°C (5 min); purge: 1 min; column pressure: 8.5 psi; split ratio: (75:1); cryotrap: from -10°C at 40°C/s to 280°C (3 min)
Gas chromatograph (GC)	Capillary column: HP-5MS (30m × 0.25 mm × 0.25 µm); column flux: 1mL/min; carrier gas: helium (99.999%); oven temperature program: from 35ºC (10 min) at 5ºC/min to 280ºC
Mass spectrometer (MS)	Transfer line to MS: 250ºC; ion source: electron impact (EI) 70 eV; ion source temperature: 200ºC; solvent cut time: 2.5 min; acquisition mode: SCAN; range of scan: 35-450 amu; electron multiplier voltage: 1.0 kV; NIST05 library

3. Results and Discussion

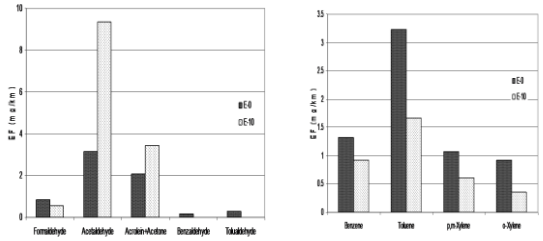
3.1. Transient Mode

3.1.1. Effect of Ethanol on Aldehydes Emissions

The aldehydes such as formaldehyde, acetaldehyde, acrolein + acetone, and aromatic aldehydes (benzaldehyde and tolualdehyde) have been selected in this study because of the three major reasons. Firstly, these species contribute maximum to the total aldehyde pollutants emanated from gasoline and gasoline-ethanol fuelled spark ignition engines [5 and references therein]. According to Pang et al. [6], formaldehyde, acetaldehyde, acrolein, and aromatic aldehydes are the dominant components which account for up to 82.2% and 85.1% of total carbonyl emissions from gasohol and gasoline fuels, respectively. Secondly, the presence of correctly operated TWC results in the oxidation of such pollutants leading to a negligible small or even zero magnitude for some of them. Thirdly and most importantly, pollutants like formaldehyde, acetaldehyde and acrolein have been declared as possible human carcinogens. According to US EPA [11], formaldehyde is a probable human carcinogen (Group B1); acetaldehyde is a possible human carcinogen (Group 2b); and acrolein is a probable human carcinogen (Group C). Moreover; Carlier et al. [12] has reported that aldehydes like formaldehyde, acetaldehyde, and acrolein are mutagenic, toxic, and even carcinogenic to human body. According to Poulopoulos et al. [13], acetaldehyde and acetone are involved in the photochemical smog generation cycle while acetaldehyde is also a toxic compound. Since, it was difficult to separate acrolein and acetone in the column because of their same retention time (almost same), so they have been discussed together in this study.

As shown in Figure 3 (a), formaldehyde decreases by 46% however, acetaldehyde and acrolein+acetone increase by about 3 times and 1.6 times, respectively in case of E-10 compared with E-0. Benzaldehyde and tolualdehyde show their significant appearance only in case of E-0 fuel.

This phenomenon of increase in acetaldehyde with a decrease in formaldehyde from E-10 as compared to E-0 is also supported by other literature [5-6]. The increase in acetaldehyde in case of E-10 is due to the oxidation of ethanol to acetaldehyde. On the other hand, the increase in formaldehyde in case of E-0 is attributed to the incomplete combustion of the gasoline fuel as compared to oxygenated gasohol fuel. According to Magnusson et al. [5], formaldehyde from the vehicle exhaust mainly comes from the inefficient combustion of saturated aliphatic and aromatic hydrocarbons frequently present in E-0. It has been reported that the presence of TWC augments the rate of oxidation of E-10 [13-14], thus results in reduced formaldehydes. The increase in acrolein+acetone in case of E-10, relative to E-0 may be ascribed to two factors. First to TWC which has shown comparatively a better efficiency in the oxidation of acrolein+acetone precursors with E0, and then to acrolein which comes mostly from the oxidation of glycerol and other residues present in the biofuels like gasohol. The absence of aromatic aldehydes (benzaldehyde and tolualdehyde) in case of E-10 is due to the less aromatic content in biofuels, relative to fossil fuels.



(a) (b)

Figure 3. Effect of Ethanol on (a) Aldehydes and (b) BTX Emissions in transient mode.

3.1.2. Effect of Ethanol on BTX Emissions

The BTX-components have been discussed in this study because of the health hazards associated with them. According to International chemical safety cards published by National Institute for Occupational Safety and Health (NIOSH) U.S.A., benzene is carcinogenic to humans and may affect the blood forming organs, liver and immune system; toluene may affect the central nervous system, resulting in decreased learning ability and psychological disorders; p,m-xylene may have effects on the central nervous system and may cause toxicity to human reproduction or development; and o-xylene may cause damage to central nervous and hearing systems [2]. It has also been reported that the exposure to benzene increases the risk of leukemia [11]. According to Poulopoulos et al. [13],benzene and toluene belong to aromatics– compounds accused of cancer generation. Furthermore, xylene isomers may convert significant amounts of NO to NO_2 [15].

As shown in Figure 3 (b), the decrease in emission factor (EF) of benzene, toluene, p,m-xylene and o-xylene is 37%, 48.3%, 43% and 71.8%, respectively.

consequently, there is a decrease of 54.4% in total BTX emissions in case of E-10 compared to E-0.

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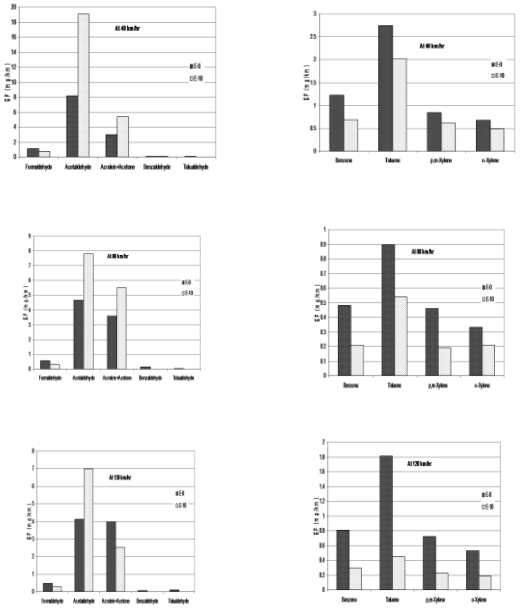
The reduction in BTX emissions is due to the oxygen enrichment in ethanol, contributing to the complete oxidation of BTX species in case of E-10, relative to E-0. According to Reuter et al. [16], benzene emissions were reduced by 10.5% with the oxygenated fuels. Besides this, physic-chemical properties like lower boiling point, faster flame propagation speed, and simple chemical structure help E-10 in the quicker development of temperature, relative to E-0. The higher temperature developed in the combustion chamber with E-10 is useful for the oxidation of BTX species. Moreover, the performance of TWC is further enhanced for the decomposition of BTX species in case of E-10, compared with E-0. This decrease in benzene and toluene with E-10 in the presence of TWC is also supported by other literature [13].

3.2. Steady Mode

3.2.1. Effect of Ethanol on Aldehydes Emissions

Figure 4 (a) shows the aldehyde emissions at three different modes of 40, 80, and 120 km/hr. Formaldehydes emitted with E-0 are dominant to those emanated with E-10 for all the steady modes. Acetaldehydes in case of E-10, on the other hand, do not show only the dominancy to those emitted with E-0, but are the most abundant components among the aldehyde species for all the steady modes. Acrolein+Acetone emissions are higher with E-10 compared to those with E-0 for the first two steady modes. However, the third mode reflects a decrease in the acrolein+acetone emissions with E-10, relative to E-0. The reasons for lower formaldehyde and higher acetaldehyde and acrolein+acetone emissions with E-10 compared to E-0 are the same as discussed earlier in the transient mode.



(a) (b)

Figure 4. Effect of Ethanol on (a)Aldehydes and (b) BTX Emissions in steady mode.

Table 3. EF of Total BTX emitted from the vehicle at different speed modes (mg/km)

Fuel	40 km/hr	80 km/hr	120 km/hr
E-0	5.49	2.17	3.87
E-10	3.80	1.15	1.17

3.2.2. Specific Reactivity

The specific reactivity is defined as the milligram (mg) ozone (O_3) potential per milligram non- methane organic gases (NMOG) emanated from the exhaust and can be evaluated as under [17]:

$$SR = \sum (NMOG_i \bullet MIR_i) / \sum NMOG_i \qquad (1)$$

The subscript i represents the certain pollutant emitted; NMOG is the sum of non-methane hydrocarbons and oxygenates, including aldehydes and BTX; and MIR is the maximum incremental reactivity. Carter and Lowi [17], examined air modeling based on ozone forming reactivates of species and proposed the MIR factor as an index for ozone formation given in appendix Table A. This index indicates the maximum increase in ozone formation

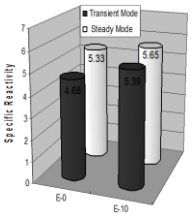


Figure 5. Specific reactivity of emissions from transient and steady modes.

Figure 5 shows the comparative SR of emissions from the vehicle at different working conditions in both transient as well as steady modes. For the steady mode, mean of the emissions at three different modes has been taken here. It is elucidated that pollutants in the transient mode of operation show less SR as compared to those emitted in steady mode. This is due to the fact that during the transient mode of operation, the total pollutants (sum of aldehydes and BTX) are less than the total mean (sum of mean) of the pollutants at steady modes as shown in Table 4. Relative to E-0, E-10 exhibits higher SR of pollutants for both transient as well as steady modes as shown in Figure 5. This higher SR in case of E-10 is ascribed to the higher acetaldehyde and acrolein+acetone emissions with gasohol, compared with gasoline.

Table 4. EF of Total pollutants at transient and mean steady state Modes (mg/km)

Fuel	Transient	Mean steady
E-0	13.13	13.90
E-10	16.90	18.28

4. Conclusions

Aldehyde and BTX emissions emanated from a TWC-retrofitted dual fuel light duty vehicle were studied in terms of their EF and SR. The vehicle was alternatively fueled with E-10 and, thus pollutants were compared with those emitted in case of baseline E-0 fuel. The experimental results showed that during the transient mode of operation, formaldehyde emissions were decreased by 46%, while acetaldehyde and acrolein+acetone emissions increased by about 3 times and 1.6 times respectively with E-10, compared with E-0. Benzaldehyde and tolualdehyde were significantly found only in case of E-0 fuel. Moreover, the benzene, toluene, p,m-xylene and o-xylene species with E-10 were decreased by 30.3%, 48.3%, 37% and 71.8% respectively, resulting in an overall decrease of 54.4% in the BTX emissions, compared with E-0.

During the steady modes, formaldehydes with E-0 were dominant to those with E-10 fuel. Acetaldehydes with E-10 showed dominancy to those with E-0, and were the most abundant components among the aldehyde species for all the steady modes. The acrolein+acetone emissions with E-10 were higher to those with E-0 for the first two modes. The formaldehyde emissions were decreased with the increase in speed in case of both E-0 and E-10 fuels. The toluene was found to be the most abundant component of the BTX emissions with both the fuels. The BTX emissions were decreased by 30.8%, 47% and 69.7% at 40, 80 and 120 km/hr respectively in case of E-10 compared to E-0. The total BTX emissions (sum of all the components) exhibited their maxima at lower speed mode and minima at medium speed mode for both the fuels.

The specific reactivity of the pollutants emitted intransient mode was less than that calculated from the mean of the three steady modes pollutants in case of both the fuels. Relative to E-0, E-10 fuel displayed the higher SR for both transient as well as steady modes of operation.

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Appendix

Table : MIR values for aldehyde and BTX emissions

BTX	MIR	Aldehydes	MIR
Benzene	0.42	Formaldehyde	7.15
Toluene	2.73	Acetaldehyde	5.52
p,m-Xylene	7.64	Acrolein+Acetone	6.77*,0.56**
o-Xylene	6.46	Benzaldehyde	-0.56
		Tolualdehyde	-0.56

6.77* is for acrolein and 0.56** is for acetone