



Investigation on characteristics of exhaust and evaporative emissions from passenger cars fueled with gasoline/methanol blends



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HIGHLIGHTS

- Dilution air refine system's advantage in purifying dilution air was confirmed.
- Both exhaust and evaporative emissions of a passenger car were investigated.
- Unregulated pollutants of evaporations from a car fueled with gasoline and M15.
- Evaporative emission characteristics from gasoline/M15 fueling car were studied.

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ABSTRACT

Exhaust and evaporative emissions including regulated and unregulated pollutants emitted from a passenger car fueled with gasoline and M15 fuel (M15 means the fuel was consisted with 85% gasoline and 15% methanol by volume) were discussed in this paper. To improve the measurement accuracy of the unregulated pollutants, the dilution air refine system (DAR) was introduced. The exhaust emission tests were performed on the chassis dynamometer, emission factors were measured by a constant volume sampling (CVS) system equipped with DAR over the New European Driving Cycle (NEDC). The evaporative emission tests were performed in the Sealed Housing for Evaporative Determination (SHED). Carbonyls, volatile organic compounds (VOCs) and methanol were sampled through the battery-operated air pumps using tubes coated with 2,4-dinitrophenylhydrazine (DNPH), Tenax TA and silica gel respectively. The test results show that comparing with gasoline operations, THC and CO from passenger car fueled with M15 decreased by 16% and 7% while the NO_x increased by 85%. The formaldehyde emitted from M15 fueling passenger car was almost two times larger than that from gasoline fueling. For the evaporative emissions, diurnal losses are far more than hot losses and turn out to be the main contributor to the evaporative emissions. For different fuels, evaporative THC from M15 increased by 63%. Given the unregulated pollutants, carbonyls and VOCs increased by 19% and 23%. Moreover, methanol from M15-fueling car was 128 times higher than that from gasoline fueling. It is important to research new canister to decrease the evaporative emissions.

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1. Introduction

The growing environmental concerns and the dual worldwide crisis of fossil fuel depletion promoted the developments of low emission vehicles (LEVs) and alternative fuels [1]. Among the alternative fuels, the excellent combustion properties of methanol and ethanol have made them been widely used as fuels for vehicles in many countries [2]. As the composition of the alternative fuels is different from the traditional fossil fuels like gasoline, the unregulated pollutants produced by alternative fuels need more attention.

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Carbonyls have received regulatory attention as toxic air contaminants, mutagens, and carcinogens. Fuel combustion is a well-known direct source of carbonyls emissions to the atmosphere [3]. Formaldehyde emitted from methanol and other alcohol fuels has become the focus. Some studies reported that formaldehyde is typically the most abundant carbonyls in combustion exhaust emissions.

Many studies have researched the unregulated pollutants emitted from the light duty vehicles fueled with alternative fuels [4–7]. However, the dilution air used in all these studies was ambient air. The concentrations of exhaust pollutants diluted by constant volume sampling (CVS) system are very close to or even lower than the background concentrations of dilution air, thus the test result

diluted by ambient air could sometimes be negative and led to backward measurement accuracy and poor repeatability [8]. As the formaldehyde emission is significantly less than the legislated pollutants, the influence of ambient air on the measurement of formaldehyde becomes more evidently. It is important and essential to improve the measurement accuracy of unregulated pollutants. Meanwhile, the LEVs put forward the demand on emissions' measurement accuracy too. So the traditional CVS system needs to refine the background air. In this paper, a dilution air refine system (DAR) is designed to solve this problem.

The tailpipe emissions are much cleaner than before with the developments of new technologies and advanced after-treatments. However, the evaporative emissions continue constituting an increasing share of total hydrocarbon (HC) emissions which need to be paid more attention. Evaporative emissions caused not only economic losses but also environment pollution. Volatile organic compounds (VOCs) from evaporative emissions are ozone precursors and contribute to ground-level ozone [9]. Mellios et al. [10] studied the breathing losses which are due to evaporation of gasoline in the tank during the real driving and parking as a result of normal diurnal temperature variation according to the current European SHED test procedure. Schifter et al. [11] studied the different characteristics of evaporative emissions from MTBE and ethanol fueling vehicles and pointed that it is important to notice an increase of about 9% in evaporative emissions with ethanol. However, few studies have investigated on evaporation from vehicles fueled with alternative fuels like methanol especially on the evaporative unregulated pollutants from methanol.

In this paper, the feature of the DAR system was introduced; the exhaust emissions and evaporative emissions including regulated and unregulated pollutants were identified and quantified. This article focused on the refining efficiency of the DAR system and the characteristics of the exhaust emissions and evaporative emissions from a passenger car fueled with gasoline and methanol/gasoline blends namely M15fuel which was consisted with 85% gasoline and 15% methanol by volume.

2. Experimental setup and measurement methods

2.1. Test car, fuel and driving conditions

The experiments were performed by using a Euro 4 standard passenger car (Inertia weight class: 1250 kg, Maximum power: 70 kW, Fuel system: multi-point injection, Displacement: 1.6L, After-treatment: three-way catalyst, Odometer: 17,591 km).

Commercial 93# gasoline was used as the base fuel. Industrial grade methanol was mixed in fractions of 15% by volume, and the fuel blends was thus named M15. The car was tested with commercial 93# gasoline first and then with M15. When the car was fueled with M15, the fuel system was not modified. When the measurement of car fueled with gasoline was finished, run the car for some time until the car was shut off automatically, and then fill the tank with some M15 and run the car again to clean the fuel system to decrease the effect in the process of fuels change.

The car was tested on the chassis dynamometer (PECD9400, Ono sokki, Japan). The cycle employed was the New European Driving Cycle (NEDC) which is the legislative test cycle in China. In this test procedure, the car was conditioned at a temperature of $25 \pm 2^\circ\text{C}$ over a time period of 16 h. The whole test lasts 1180 s. The dilution system consists of traditional CVS system (7200S, Horiba, Japan) and the new CVS system equipped with DAR system (1400, Horiba, Japan) which is named DAR-CVS system.

2.2. Sampling and analysis

The schematic diagram of the measurement system for vehicle exhaust emissions is illustrated in Fig. 1. According to the test standard, the pollutants sampled in the airbags were analyzed by the motor exhaust gas analyzer (MEXA-7400LE, Horiba, Japan) in 20 min after the test cycle. The resolution time of the motor exhaust gas analyzer is lower than 1.5 s. In order to ensure that the exhaust gas analyzer was sealed well and the test results were with satisfied accuracy, the gas analyzer should pass the leak test and be calibrated by using of propane gas before sampling and analyzing.

In the test procedure, the exhaust emissions were diluted by CVS and DAR-CVS respectively.

Carbonyls from the CVS-diluted (or DAR-CVS-diluted) exhaust can be collected through a battery-operated air pump (Aircheck2000, SKC, USA) using 2,4-dinitrophenylhydrazine(DNPH)-coated silica cartridges (Supelco, USA) and analyzed by high performance liquid chromatography (HPLC1200, Agilent, USA) using a variable wavelength detector. Table 1 shows the analysis conditions of the HPLC.

VOCs are defined as the general term for all the organic compounds whose boiling points were between 323 K and 633 K under the normal pressure. In this paper, the targets VOCs contain benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, styrene, n-butylacetate, and n-undecane. Due to difficulties in resolving the chromatography peaks, the results for m-xylene and p-xylene are represented as a sum.

VOCs were sampled through a battery-operated air pump using stainless steel sorbent tubes coated with Tenax TA (Markes, UK) and then analyzed by thermal desorption (Markes, UK) and identified by gas chromatography with a mass spectrometer detector (GC/MS, Agilent, USA). The analysis conditions of the VOCs are listed in Table 2.

Methanol was sampled through a battery-operated air pump using solid sorbent tubes coated with silica gel (Supelco, USA) and analyzed by the gas chromatography with a flame ionization detector. Table 3 shows the analysis conditions.

Identifications of the unregulated pollutants were made by matching retention time with those of commercial standard mixtures. And the quantifications were obtained by the five-point external standard method with which the correlation coefficients of the linear calibration curves for each unregulated pollutants were more than 99.9%.

2.3. Evaporative emissions test procedure

Evaporative emissions tests were performed in sealed housing for evaporative determination (SHED) designed for performing vehicle certification tests by AVL. The total system of SHED consists of the chamber, electrical control cabinet, volume compensation module, temperature conditioning module, temperature chilled water module, canister conditioning system, fuel tank heating system and analytical system.

Evaporative emissions from vehicles are generally divided into five categories namely: diurnal losses, hot-soak losses, running losses, resting losses and refueling losses. According to the Chinese legislation, this study focuses on hot-soak losses and diurnal losses. Hot soak losses are those generated after a vehicle has been shut off after driving. Diurnal losses originate from the vehicle fuel tank as the fuel evaporates due to the daily ambient temperature variations.

To determine the evaporative emissions, the vehicle needs to be placed inside the SHED. The sampling system feeds a continuous sample of the mixed SHED air to a flame ionization detector (FID) gas analyzer with the resolution time lower than 1.5 s. Thus

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