

Research on Unregulated Emissions from an Alcohols-Gasoline Blend Vehicle Using FTIR, HPLC and GC-MS Measuring Methods

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ABSTRACT

Unregulated emissions have become an important factor restricting the development of methanol and ethanol alternative alcohols fuels. Using two light-duty vehicles fuelled with pure gasoline, gasoline blend of 10% and 20% volume fraction of ethanol fuels, gasoline blend of 15% and 30% volume fraction of methanol fuels, New European Driving Cycle (NEDC) emission tests were carried on a chassis dynamometer according to ECE R83-05. High performance liquid chromatography (HPLC), Gas chromatography - Mass spectrometry (GC-MS), Fourier transform infrared spectrometer (FTIR) were used to measure methanol, formaldehyde, acetaldehyde, acetone, benzene, toluene, xylene, ethylene, propylene, 1,3-butadiene and isobutene emissions in the exhaust during the NEDC.

The test results show that the methods of the integration of FTIR instantaneous values and the chemical analysis of bag sampling can both accurately measure formaldehyde, acetaldehyde, and benzene and toluene emissions in the vehicle exhaust. Comparing the instantaneous emissions and average emissions during the driving cycle of major pollutants, the good consistency of FTIR, HPLC and GC-MS measuring methods has been verified. The emissions deviations of various measurement methods are in the range of $\pm 10\%$.

During the first acceleration condition, the instantaneous emissions of methanol, formaldehyde, acetaldehyde, benzene, propylene and 1,3-butadiene have the highest peak. Then with the three-way catalyst lights off, the emissions values gradually reduce to nearly zero and remain until the end of the driving cycle.

As the alcohols proportion increasing in the fuel, CO₂ emissions in the exhaust remain basically the same, HC, CO and CH₄ emissions decrease slightly, NO_x emissions increase slightly, unburned methanol, formaldehyde and acetaldehyde emissions increase proportionally, benzene, toluene, ethylene, propylene, 1,3-butadiene and isobutene emissions decrease.

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INTRODUCTION

With the gradual depletion of petroleum resources worldwide, developing alternative energy sources become a more urgent task all over the world. European car manufacturers research and development organizations in 2004 carried out a performance evaluation for kinds of motor vehicle fuels and power systems for the entire life cycle (well-to-wheel)^[1], which made a forecast that the automobile industry in the coming decades would be a diversification development of the fuel and the power system. Ethanol is a biomass fuel, which has the advantage of a wide range of

sources. It could be produced from the raw materials of starch, sugar and cellulose. Currently as one of the most used biomass alternative fuels, ethanol is used in gasoline vehicles mainly in the form of blending with gasoline. The application of ethanol fuel has succeeded in marketization especially in Brazil and the United States^[2]. The pilot run of E10 ethanol-gasoline fuel has also been carried out in more than ten provinces of China. According to China's "oil-poor, gas-little, coal-rich" structure of energy resources, to promote the development of coal-based methanol fuel as a clean alternative to gasoline fuel is one of the most realistic

options. China has utilized the life cycle method to carry out the assessment of the feasibility of the application of methanol fuel^[3]. From 2012 a pilot run of vehicles fuelled with M85 and M100 high percentage of methanol fuels has been carried out in Shanxi Province, Shanghai and Shaanxi Province.

With gradually promoting the application of alternative fuels, the problem of unregulated emissions from methanol-gasoline and ethanol-gasoline vehicles has been paid more attention. Blending methanol or ethanol fuels in existing gasoline vehicles, CO and HC emissions in the exhaust will reduce in a certain extent, due to the oxygen content contained in the fuel^[4,5]. However, a large amount of methanol, formaldehyde, acetaldehyde, acetone, benzene and toluene emissions may be emitted, as the incomplete combustion of methanol or ethanol fuels occurs^[6,7,8]. These polycyclic aromatic hydrocarbons, aldehydes and ketones pollutants have a very strong stimulation and sensitization, as well as potential genetic toxicity and carcinogenic activity, which have a great impact on human health.

Existing literatures show that many automobile companies and research institutions have carried out qualitative and quantitative analysis on unregulated emissions. Different measurement methods were utilized to measure various unregulated emissions from methanol and ethanol engines and vehicles. For example, in Xi'an Jiaotong University^[9], Tianjin University^[10] and Jilin University^[11] unburned methanol and formaldehyde emissions from methanol-gasoline engines were measured by GC. In Chrysler Motor Company^[6], The American auto testing laboratory^[12] and Beijing Institute of Technology^[13], HPLC and GC-MS were used to measure benzene and formaldehyde emissions during the driving cycle from methanol-gasoline vehicles. In Tsinghua University^[14], methanol, formaldehyde and acetaldehyde emissions before and after the catalyst from methanol-gasoline engines were also measured by FTIR. In Xi'an Jiaotong University^[15], Tsinghua University^[16], Tianjin University^[17] and the Massachusetts Institute of Technology^[18], GC were used to measure formaldehyde, acetaldehyde and ethanol emissions from ethanol-gasoline engines. In the French Institute of Petroleum^[19], acetaldehyde and aromatic hydrocarbon emissions in the exhaust from ethanol vehicles were measured by GC-MS. FTIR were also used to measure the instantaneous emissions of formaldehyde, acetaldehyde and benzene from ethanol-gasoline vehicles in different cycle conditions in Austria AVL company and the Finnish National Technology Research Center^[20]. Overall, the measurement methods of these researches were different and the measurement objects were relatively scattered. Thus, a comprehensive and systematic conclusion is lacking.

In accordance with the EU R83-05 standard, emissions testing of the NEDC were carried out in a light-duty vehicle chassis dynamometer. Using FTIR, HPLC and GC-MS joint research methods unregulated emissions were measured from same light-duty vehicles fuelled with different proportional methanol and ethanol gasoline fuels. Firstly, CO, CO₂, NO_x, formaldehyde, acetaldehyde, benzene and toluene emissions results measured by different testing methods were comparatively analyzed. The accuracy and consistency of the FTIR, HPLC and GC-MS measuring methods were verified. The influences of methanol and ethanol proportions in fuels on methanol, formaldehyde, acetaldehyde, acetone, benzene, toluene, xylene, ethylene, propylene, 1,3-butadiene and isobutylene emissions were research through the joint measuring methods.

EXPERIMENT SETUP

Tested Fuels

Tested gasoline is 93# China IV standard fuel provided by Yanshan Petrochemical Company. Tested methanol is high-purity industrial methanol bought from Yanlan petrochemical company. Tested ethanol is anhydrous ethanol (AR) bought from Sinopharm Chemical Reagent Co., Ltd. The ethanol content is more than 99.7%. Before the test 10% and 20% volume fraction of ethanol were blended with gasoline. After sufficient stirring E10 and E20 ethanol gasoline fuels were obtained. Similarly, M15 and M30 methanol gasoline fuels were obtained by blending 15% and 30% volume fraction of methanol with gasoline. Fuels in the vehicle were firstly emptied and then 20L of pure gasoline, M15, M30, E10, E20 fuels were added into the vehicle in turn to carry out the test. After the test the remaining fuels in the vehicle were release off and then 2L of fuel samples were sent to SGS test center and analyzed. The analysis results of the parameters of pure gasoline, methanol gasoline, and ethanol gasoline fuels are shown in [Table 1](#).

Table 1. Key parameters of tested fuels

Fuel Name	Gasoline	M15	M30	E10	E20
Density (g/cm ³)	0.769	0.768	0.766	0.759	0.763
RON	94.2	98.5	101.5	97.4	99.0
Vapor Pressure (kPa)	55.4	57.4	65.2	53.2	49.3
Alcohols Content (%)	0.1	14.3	30.03	8.73	18.85

Tested Vehicles

The tested vehicles are two 2011 year 1.6L AT light-duty vehicles of the same model. The mileage of 1# tested vehicle is approximately 11,000 kilometers and 2# tested vehicle is 22,000km. 1# tested vehicle used pure gasoline, M15, and M30 fuels. 2 # tested vehicle used pure gasoline, E10, and E20 fuels. The parameters of tested vehicles are shown in [Table 2](#).

Table 2. Key parameters of tested vehicles

Curb Weight (kg)	1285
Displacement (L)	1.6
Engine Type	Naturally aspirated
Maximum Power (kW)	77
Maximum Torque (N·m)	155
Fuel Label	93#
Emission Standard	Euro IV + OBD

Experimental Facilities

The testing system is made up of chassis dynamometer system, environmental simulation system, emission analysis system, control system and other components. The types of test devices and instruments are shown in Table 3. Type ECDM-48L-4WD light-duty vehicle emissions chassis dynamometer of the German MAHA company is used in the test. The exhaust gas analysis system in the test includes CVS-7400 constant volume sampling system, MEXA-7400 regulated emissions analysis system, and MEXA-6000FT multi-component emissions analyzer of the Japanese Horiba Company. The environment simulation system includes SFTP low temperature environmental testing chamber of the German IMTECH company and DAR-3300 air purification system of Horiba Company.

Table 3. Types of test devices and instruments

Device Name	Instrument Type	Production Company
Chassis Dynamometer	ECDM-48L-4WD	German MAHA
Environmental Testing Chamber	SFTP	German IMTECH
Constant Volume Sampling System	CVS-7400	Japanese HORIBA
Regulated Emissions Analysis System	MEXA-7400LE	Japanese HORIBA
Multi-component Emissions Analyzer	MEXA-6000FT	Japanese HORIBA
Air Purification System	DAR-3300	Japanese HORIBA

MEASURING METHODS

Instantaneous and cycle average emissions of regulated and unregulated pollutants in the vehicle exhaust were measured by joint methods of MEXA, FTIR, HPLC, and GC-MS.

Instantaneous Emissions

Instantaneous regulated emissions were measured by two kinds of methods: MEXA-7400LE (MEXA method) and MEXA-6000FT (FTIR method).

In MEXA method the sampling object is the diluted exhaust gas, which has mixed with the dilution air in the mixing chamber. In the MEXA-7400LE system the instantaneous values of CO and CO₂ emissions are measured by NDIR (Non-Dispersive Infrared) analyzer. Instantaneous NO_x emission is measured by CLD (Chemiluminescent detector) analyzer. HFID (Heated flame ionization detector) analyzer is used to measure the instantaneous value of HC emission. The measurement results are marked as CO(MEXA), NO_x(MEXA), CO₂(MEXA), and HC(MEXA).

In FTIR method instantaneous values of CO, NO_x, CO₂, and CH₄ emissions in the vehicle exhaust before the mixing chamber are measured using MEXA-6000FT. According to the method specified in the EU R83-05 standard, the instantaneous dilution factor is calculated by instantaneous CO₂, HC and CO emissions values, which are obtained from the MEXA-7400LE system. Through the factor the FTIR measured concentration is converted into the concentration in the diluted exhaust gas, respectively marked as CO(FTIR), NO_x(FTIR), CO₂(FTIR), and CH₄(FTIR).

The instantaneous emissions of CH₃OH, HCHO, CH₃CHO, C₆H₆, C₇H₈, C₂H₄, C₃H₆, 1,3-C₄H₆, and iso-C₄H₈ unregulated pollutants before the dilution are measured by MEXA-6000FT (FTIR method).

Cycle Average Regulated Emissions

The cycle average emissions of regulated pollutants are calculated by three kinds of methods: MEXA analysis of bag sampling, integral of FTIR instantaneous values, and integral of MEXA instantaneous values.

In MEXA analysis of bag sampling method, regulated emissions of CO, NO_x, HC, and CH₄ pollutants of diluted exhaust gas in the sampling bag are measured MEXA-7400LE at the end of the driving cycle. The results are marked as MEXA analysis results of bag sampling.

In the integral of FTIR instantaneous values method, the cycle average emissions are calculated by integrating the instantaneous emissions curve. According to the EU R83-05 standard, the instantaneous flow of the diluted exhaust gas is recorded by the constant volume sampling system. The integral of above FTIR instantaneous emissions results and the instantaneous flow is calculated. The average emissions values of CO, NO_x, CO₂, and CH₄ pollutants during the cycle are obtained by dividing the total vehicle driving distance. The results are marked as the integral results of FTIR instantaneous values.

Similarly in the integral of MEXA instantaneous values method, the average emissions of CO, NO_x, CO₂, and HC pollutants during the entire NEDC are obtained by the integral of the MEXA instantaneous emissions results and the instantaneous exhaust gas flow, marked as the integral results of MEXA instantaneous values.

Cycle Average Unregulated Emissions

The cycle average emissions of unregulated pollutants are measured by two kinds of methods: the integral of FTIR instantaneous values and chemical analysis of bag sampling.

Similarly as CO, NO_x, CO₂, and CH₄ pollutants, the average emissions of formaldehyde, acetaldehyde, benzene, toluene, methanol, ethylene, propylene, 1,3-butadiene, and isobutylene pollutants during the NEDC are obtained by the integral of FTIR instantaneous values method.

In the chemical analysis of bag sampling method, unregulated emissions of the diluted exhaust gas in the sampling bag are measured by the chemical analysis method from the dilute exhaust bag after the NEDC. At the end of the testing cycle, TENAX-TA adsorption columns are used to sample VOCs (Volatile organic compounds) in the diluted exhaust gas and 2,4-DNPH adsorption columns are used to sample aldehydes and ketones pollutants. After the thermal desorption of TENAX-TA absorption columns, GC-MS are used to obtain benzene, toluene, and xylene emissions. After the solid phase extraction of 2,4-DNPH adsorption columns, formaldehyde, acetaldehyde, and acetone emissions can be obtained by HPLC. In order to avoid the interference of sampling and analysis process in the test results, the same diluted exhaust gas were sampled twice in the test. The samplings are independently analyzed in the China Automotive Technology & Research Center and the Beijing Physical and Chemical Analysis Center. The measurement results are marked as the chemical analysis results (bag sampling 1) and chemical analysis results (bag sampling 2).

RESULTS AND DISCUSSIONS

Methods Comparison

In order to verify the accuracy and consistency of the various measurement methods, instantaneous emissions of CO, CO₂, and NO_x pollutants as well as cycle average emissions of CO, CO₂, NO_x, formaldehyde, acetaldehyde, benzene, and toluene pollutants are compared.

Instantaneous regulated emissions

Comparatively analysis of the measurement results of M30 and E20 fuels, the instantaneous emissions curves of CO, NO_x, and CO₂ during the entire NEDC are measured by MEXA and FTIR two kinds of methods, as shown in Figure 1(a)~(c) and Figure 2(a)~(c).

As shown in Figure 1(a)~(b) and Figure 2(a)~(b), for either M30 fuel or E20 fuel, the curve shape and numerical size of CO and NO_x instantaneous emissions curves measured by two methods are basically the same. Even during the first 100s when the variation of emissions is largest and the last 200s when the change of vehicle speed and load is largest, CO and NO_x emissions results of two methods could accurately reflect the concentration of vehicle exhaust emissions varying with vehicle running conditions. The consistency of the two methods can be verified.

Shown in Figure 1(c) and Figure 2(c), CO₂(FTIR) is slightly bigger than CO₂(MEXA) during the entire NEDC. The reason is that the sampling objects of the two methods are different. The measuring object in FTIR method is the direct vehicle exhaust, while the sampling object in MEXA method is the diluted exhaust gas. The variation of emission peaks reduces slightly during the mixing process. Thus, the instantaneous emissions measurement results in FTIR method are slightly higher than those in MEXA method, especially CO₂ which has the biggest emission values.

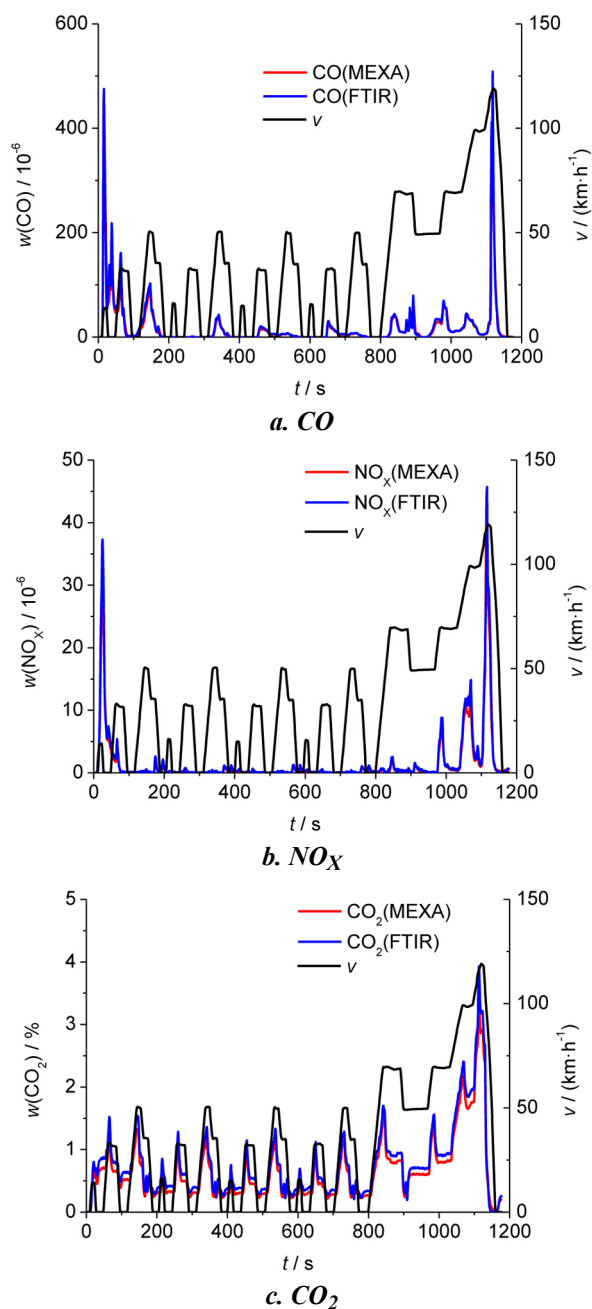


Figure 1. Instantaneous emissions curves of regulated pollutants of M30 fuel (MEXA and FTIR methods)