Fuel 148 (2015) 9–15

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Comparative study on measurements of formaldehyde emission of methanol/gasoline fueled SI engine

Peng Geng [a,b], Hui Zhang [b,c], Shichun Yang [d,*], Chunde Yao [a,*]

[a] State Key Laboratory of Engines, Tianjin University, Tianjin 300072, China
[b] Merchant Marine College, Shanghai Maritime University, Shanghai 201306, China
[c] Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, OH 43210, USA
[d] School of Transportation Science and Engineering, Beihang University, XueYuan Road No. 37, HaiDian District, Beijing 100191, China

HIGHLIGHTS

- The measurement methods applied to measure HCHO emission from engines were investigated.
- HCHO emission from an SI engine fueled with different blending ratio was measured.
- Three different methods are proposed to measure the HCHO emission from SI engines.
- Interior reasons of differences on experimental results were analyzed.

ARTICLE INFO

Article history:
Received 9 November 2014
Received in revised form 21 January 2015
Accepted 22 January 2015
Available online 7 February 2015

Keywords:
Vehicles
Formaldehyde
Fourier transform infra-red (FTIR)
High performance liquid chromatography (HPLC)
Gas chromatography (GC)

ABSTRACT

The formaldehyde emissions are harmful to human health. It is necessary to investigate and standardize the measurement methods of formaldehyde emissions from vehicles. Based on the principle of different measurements, this study proposes three different measurement methods of formaldehyde emissions from a Spark-Ignition (SI) engine fueled with 0%, 15% and 45% of methanol in volume respectively for M0, M15 and M45. Fourier transform infra-red (FTIR), high performance liquid chromatographic (HPLC) and gas chromatographic (GC) were used to measure the formaldehyde emissions from the test engine on the same engine conditions. Experimental results show that different measurement methods yield significant different results of the formaldehyde emissions, while all the measurements have the consistent trend in the change of formaldehyde emissions when the test engine operates on the different conditions. The formaldehyde emissions measured by FTIR are more than these measured by HPLC and GC, while there were slight differences on the experimental results by the use of HPLC and GC. There are three major factors leading to the different measurement results, respectively for the differences in the spectral characteristics, interferences of other exhaust emissions and the calibration of the tested gas. Compared with FTIR, chromatographic measurements present better separation of formaldehyde emissions with high frequency response, repeatability and good linearity. The formaldehyde emissions could be measured on-line by the use of FTIR, while formaldehyde emissions measured by the chromatographic measurements are absorbed into the 2,4-dinitrophenylhydrazine solution and then detected by the use of GC and HPLC offline. Therefore, HPLC and GC are preferred as the basements on the measurement of formaldehyde emissions, while FITR is preferred as an in-vehicle application.

1. Introduction

As the clean and renewable alternative fuels, several kinds of alcohol fuels could reduce the regulate emissions when applied on the vehicles [1–6]. However, the use of alcohol in the vehicles could also lead to the increase of unregulated emissions such as formaldehyde and acetaldehyde [7–12]. Formaldehyde was usually measured by chromatography or infra-red spectroscopy and so on [13–17]. In the previous studies, some researchers measured the formaldehyde emissions from the vehicles using the high-performance liquid chromatography (HPLC), the Fourier transform infrared spectroscopy analyzer (FTIR) and gas chromatography (GC) [18–20]. And other researchers used a small Sep-Pak pillar coating with 2,4-dinitrophenylhydrazone (DNPH) to absorb the

* Corresponding authors. Tel.: +86 13522187088; fax: +86 22 2740 6649.
E-mail addresses: yangshichun@buaa.edu.cn (S. Yang), arcdyao@tju.edu.cn (C. Yao).

http://dx.doi.org/10.1016/j.fuel.2015.01.075
0016-2361/

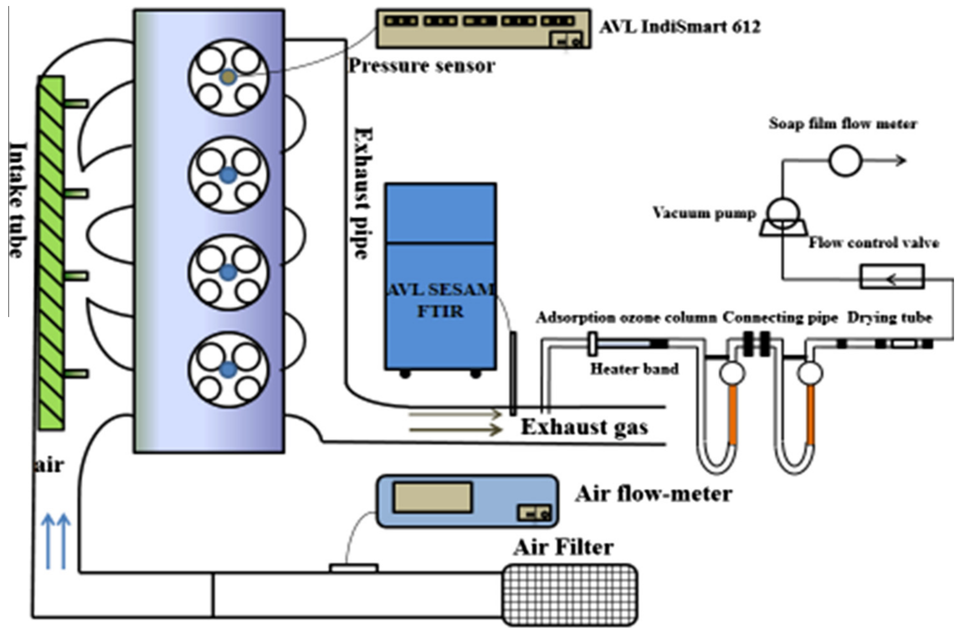

Fig. 1. Schematic of experimental system.

Table 1
Main technical specifications of tested engine.

Type of the engine	4 Stroke SI
Compression ratio	10.5
Cylinder volume	0.375 L
Bore	77.4 mm
Stroke	79.5 mm
Minimum fuel consumption rate	260 g/kW h
Maximum power	80 kW/6000/r min^{-1}
Maximum torque	140 N m/4500/r min^{-1}

Table 2
Properties of methanol and ultralow sulfur gasoline (ULSG).

Property	Methanol	ULSG
RON	106–115	92.8
Density @20 °C(kg/m^3)	792	757.6
Vapor (kpa)	12.9	44.0
Latent heat (kJ/kg)	1110	314
Sulfur content (mg/kg)	–	8
Auto-ignition temperature (°C)	437	420
Lower heating value (MJ/kg)	19.7	44.0

carbonyl compounds in the exhaust emissions [21]. The carbonyl compounds in the exhaust emissions were eluted by the use of acetonitrile. Then these carbonyl compounds were measured by HPLC with ultraviolet (UV) detector [22]. Recently, the U.S. environmental protection agency has used the HPLC to analysis the formaldehyde emissions and other carbonyl compounds from the vehicles [23]. Moreover, formaldehyde emissions were detected by FID method. [24] In this method, formaldehyde was also collected impregnated with DNPH and converted to the 2,4-dinitrophenylhydrazone derivative. In the past years, pulsed discharge helium ionization detector (PDHID) was developed, which is a low-cost chromatographic method [25–27].With the development of oxygenated fuels, such as methanol, ethanol, Di Methyl Ether (DME), Di Methyl Carbonate, biodiesel, engine and environment scholars have focused on the unregulated emissions from the vehicles [28–30]. Therefore, it is necessary to investigate and standardize the measurement methods of formaldehyde emissions from vehicles. Furthermore, with the development of the new technologies such as FTIR, the formaldehyde emissions could be measured online for engine bench test [31]. However, different measurement methods might lead to the differences in the experimental results of the formaldehyde emissions due to the different measurement principles. The analysis on the differences of experimental results and the internal relations on the different measurement methods are rarely reported.

In this study, the formaldehyde emissions from a spark-injection (SI) engine fueled with methanol/gasoline fuels are measured by three different measurement methods, respectively for FTIR, GC and HPLC. The FTIR named AVL SESAM FTIR was used to measure the formaldehyde emissions online, while formaldehyde emissions measured by the chromatographic measurements are absorbed into the 2,4-dinitrophenylhydrazine solution and then detected by the use of GC (SP3420) and HPLC (SY-8100) offline. The experimental results of the formaldehyde emissions are compared and the internal relations on the different measurement methods are analyzed. The differences in the spectral characteristics, interferences of other exhaust emissions and the calibration of the tested gas are the three major factors leading to the different results of formaldehyde emissions from the vehicle at the same engine load. This work is important and the standardization of measurement on the formaldehyde emissions is important for the development of methanol application in the vehicles.

2. Experimental apparatus

2.1. Test bench setup

The schematic of the experimental setup is shown in Fig. 1. The engine used for this study was a four-cylinder, naturally aspirated, water-cooled, Spark-Ignition (SI) gasoline engine, with

Table 3
Effect on HCHO by the flow rate of the sampling.

Flow rate (L/min)	HCHO/(10^{-6})
0.12	24
0.15	19
0.20	15