



Full Length Article

Detection and analysis of formaldehyde and unburned methanol emissions from a direct-injection spark-ignition methanol engine



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ABSTRACT

A sampling system to collect exhaust emissions of a methanol engine by means of a sampling bag and an absorber was designed to absorb formaldehyde and unburned methanol emissions with deionized pure water. Three novel measurement methods that combine gas chromatography and liquid chromatography (GCLC), gas chromatography and the light spectrum (GCLS), and liquid chromatography and light spectrum (LCLS) were used to separate and measure formaldehyde and unburned methanol emissions. The three measurement methods of GCLC, GCLS and LCLS proved suitable and reliable to separate and measure the formaldehyde and unburned methanol emissions from a direct-injection spark-ignition methanol engine. The effects of methanol injection timing, spark timing, and excess air ratio on formaldehyde and unburned methanol emissions were analyzed experimentally by measurement method of GCLS. The formaldehyde and methanol detection limits are 0.16 µg/mL and 0.18 µg/mL for gas chromatography (GC), respectively, the detection limit for methanol is 0.15 µg/mL for liquid chromatography (LC), and the detection limit for formaldehyde is 0.21 µg/mL for light spectrum (LS). Retarding the spark timing increases the formaldehyde emission and decreases the unburned methanol emissions. The formaldehyde emission decreases rapidly and the unburned methanol emission increases significantly with an increasing excess air ratio.

1. Introduction

A reduction of pollutant emissions to improve air quality and a decrease in fuel consumption because of the depletion of fossil resources are the main challenges in the automotive field [1–3]. Therefore, there is strong motivation to investigate alternative fuels for different applications, such as motor vehicles [4–6]. Methanol is considered to be one of the most favorable fuels for engines in future because it can be produced from coal, natural gas, and biomass with a relatively low cost [7–9]. However, the formaldehyde and unburned methanol emissions of methanol engines are much higher than those of traditional fuel engines [10,11]. Formaldehyde has been classified as a likely carcinogen by the U.S. Environmental Protection Agency and workplace exposure is strictly regulated. Formaldehyde is a colorless, highly toxic, and flammable gas at room temperature and it is slightly heavier than air. It has a pungent, highly irritating odor that is detectable at low concentrations (below 1 ppm). It dissolves easily in water and is found in formalin (a solution of formaldehyde, water, and

methanol). Formaldehyde is an eye, skin, and respiratory-tract irritant [12]. Formaldehyde vapor can produce a narrowing of the bronchi and an accumulation of fluid in the lungs. Low-dose acute exposure of formaldehyde can result in headaches, rhinitis, and dyspnea; higher doses may cause severe mucous membrane irritation, lacrimation, and lower respiratory effects such as bronchitis, pulmonary edema, or pneumonia. Ingestion of as little as 30 mL of a solution that contains 37% formaldehyde has been reported to cause death in an adult [13]. The lowest level at which many people can begin to smell formaldehyde is 0.05 ppm and the highest level is 1 ppm [14]. Formaldehyde plays a major role in photochemical reactions in the troposphere [11].

Methanol is the simplest alcohol, and is a light, volatile, colorless, flammable liquid with a distinctive odor that is very similar to that of ethanol (drinking alcohol) [15]. However, unlike ethanol, methanol is highly toxic and is unfit for consumption. At room temperature, it is a polar liquid, and is used as an antifreeze, solvent, fuel, and as a denaturant for ethanol. Methanol is poisonous to the central nervous system and may cause blindness, coma, and death. However, in small amounts,

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methanol is a natural endogenous compound found in normal, healthy human individuals, concluded by one study which found a mean of 4.5 ppm in the exhaled breath of subjects [16]. Methanol has a high toxicity in humans. If as little as 10 mL of pure methanol is ingested, for example, it can break down to formic acid, which can cause permanent blindness by destruction of the optic nerve, and 30 mL is potentially fatal [17], although the median lethal dose is typically 100 mL (i.e., 1–2 mL/kg body weight of pure methanol) [18].

Formaldehyde is usually monitored in the environment with the use of 2,4-dinitrophenylhydrazine (DNPH) cartridges and ultraviolet-high performance liquid chromatography (UV-HPLC) analysis [19]. Commonly used measurements methods in the environment for formaldehyde also include spectrophotometry [20,21], fluorimetry [22], laser-induced fluorescence [23], gas chromatography (GC), and HPLC [24–27]. Dojahn et al. [28] developed a new method to detect and characterize formaldehyde by GC by using a pulsed-discharge photo-ionization detector. The pulsed-discharge photo-ionization detector is used to differentiate between and identify formaldehyde and three other compounds in a simple mixture quantitatively.

Wei et al. [29] measured formaldehyde and methanol emissions from a gasohol engine by GC with a Gs-Oxy PLOT capillary column and pulsed-discharge helium ionization detector. Formaldehyde and methanol were well separated and responded linearly to the pulsed-discharge helium ionization detector within the range of 0.8–800 µg/L. Lv et al. [30] demonstrated a measurement approach for unregulated pollutants from spark ignition engine fuelled with gasoline-methanol blends by using PEG column of GC2010. The retention time for peak of formaldehyde and methanol under measurement method of GC is 4.676 min and 4.443 min, respectively. The overlap of retention time for chromatographic peak area of formaldehyde and methanol is approximately 10%–20%. This will seriously affect the measurement accuracy of formaldehyde and methanol. Geng et al. [31] compared three different measurement methods (Fourier transform infra-red (FTIR), HPLC, and GC) of formaldehyde emissions from a methanol/gasoline-fueled spark-ignition engine. They found that the formaldehyde emissions measured by FTIR exceeded those measured by HPLC and GC. The U.S. Environmental Protection Agency has recommended an HPLC method to analyze for formaldehyde and other carbonyl compounds from vehicles [32]. Formaldehyde for this method was collected on 2, 4-DNPH cartridges and eluted using HPLC-grade acetonitrile into autoinjector vials with an UV detector. Formaldehyde detection requires more than 1 h for the derivation, elution, extraction, and detection of DNPH hydrazine [33]. In these methods, FTIR can detect formaldehyde and other emissions online, and other measurement methods are offline. Therefore, those measurement methods for formaldehyde and unburned methanol emissions are more suitable for low-percent methanol/gasoline blends spark-ignition engines [34].

Previous research on the measurement of formaldehyde or formaldehyde and unburned methanol emissions have focused mainly on gasoline, diesel, gasoline/methanol blends, and diesel/methanol blends in engines [35–38]. Limited research exists on the measurement methods of formaldehyde and unburned methanol emissions in methanol engines [39,40]. The aim of this study was to develop a novel measurement method that combines GC and liquid chromatography (LC) or the light spectrum (LS) of formaldehyde and unburned methanol emissions in pure methanol engines. This study is important to standardize measurement methods for formaldehyde and unburned methanol emissions and to develop the application of methanol in vehicles.

Main novelty of this study lies on the fact that, in contrast with most the previously measurement methods, measurement methods which combine GC and LC (GCLC), GC and LS (GCLS), and LC and LS (LCLS) were used to separate and measure formaldehyde and unburned methanol emissions in the methanol engines. This would be more accurate in separating formaldehyde and unburned methanol emissions from the methanol engines.

Table 1
Specifications of the test engine.

| | |
|---------------------------------|---------------|
| Bore (mm) | 82.5 |
| Stroke (mm) | 84.2 |
| Displacement (cm ³) | 1798 |
| Compression ratio | 9.6:1 |
| Maximum power/speed (kW/rpm) | 118/5000–6200 |
| Maximum torque/speed (Nm/rpm) | 250/1500–4200 |

Table 2
Properties of gasoline and methanol.

| Property | Methanol | Gasoline |
|-------------------------------------|--------------------|--------------------|
| Formula | CH ₃ OH | C ₅ -12 |
| Molecular | 32 | 95–120 |
| Oxygen content (% mass) | 50 | 0 |
| Density (kg/m ³) | 790 | 720–780 |
| Viscosity at 20 °C (mPa·s) | 0.34 | 0.6 |
| Boiling point (°C) | 65 | 30–220 |
| Flash point (°C) | 11 | – 45 |
| Research octane number | 111 | 80–98 |
| Flammability limit (% volume) | 6.7–36 | 1.47–7.6 |
| Latent heat of vaporization (kJ/kg) | 1110 | 310 |
| Lower heating value (MJ/kg) | 19.6 | 44.5 |
| Auto ignition temperature (°C) | 470 | 228–470 |
| Stoichiometric air–fuel ratio | 6.5 | 14.7 |
| Flame speed (m/s) | 0.523 | 0.38 |

2. Experimental setup

Experiments were conducted on an in-line four-cylinder, four-stroke, water-cooled, direct-injection spark-ignition gasoline engine. Specifications of the test engine are shown in Table 1. The properties of gasoline and methanol that were used for this test with a purity that exceeded 99% are shown in Table 2 [8,41].

The experimental system is shown in Fig. 1. The methanol injection timing, spark timing, and throttle-valve opening degree were adjusted by using a self-developed electronic control unit. The excess air ratio was measured by using an ETAS Lambda Meter LA4 oxygen sensor. An electric eddy dynamometer was coupled to measure engine speed and torque. This experimental setup has been used in previously works [42]. A sampling bag was used to collect exhaust gas. Measurement error analysis is given in Table 3.

During the test, the intake temperature was 18 °C, the intake pressure was 99 kPa, the spark duration was 0.03 ms, the spark power was 50 mJ, the injection mass per cycle was 63 mg/cycle, the engine speed was 2500 rpm, the engine brake mean effective pressure was approximately 0.26 MPa, and the throttle-valve opening degree was fixed at 8°.

3. Detection of formaldehyde and unburned methanol

3.1. Sampling methods

The following four sampling methods were used:

(1) Direct sampling

Engine exhaust from the exhaust pipe enters the gas chromatograph directly to measure the amount of formaldehyde and unburned methanol by a sampling device. In this sampling method, gas samples remained untreated, and the material in the exhaust changed minimally. However, this method requires a long sampling time (approximately 30 min) to measure formaldehyde and unburned methanol. For samples of a lower concentration, the direct sampling accuracy is low.

(2) Bag sampling

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