Study on the development status and emission levels of methanol vehicles

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Abstract. Based on the research on the development status of methanol vehicles and formaldehyde testing technology at home and abroad, a comparison test was conducted between National V gasoline vehicles and methanol vehicles, and it was found that CO and THC emissions of methanol vehicles are lower than those of gasoline vehicles, NOx emissions are roughly the same as those of gasoline vehicles, and PM emissions are significantly lower; formaldehyde emissions are higher than those of gasoline vehicles. However, the existing testing methods cannot achieve direct and continuous testing of formaldehyde, and there is an urgent need to develop a direct measurement method for formaldehyde and corresponding testing equipment for in-use methanol-fuelled vehicles.

Keywords: Methanol, Emission levels, Formaldehyde.

1 Introduction

According to the Ministry of Ecology and Environment of the People’s Republic of China, in 2021, the number of motor vehicles in China will reach 395 million, and the total emissions of four pollutants from motor vehicles will be 15.577 million tonnes, of which carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NOx) and particulate matter (PM) emissions will be 7.683 million tonnes, 2.004 million tonnes, 5.821 million tonnes and 6.9 million tonnes respectively. With automobiles still being the main contributor to total pollutant emissions, emitting more than 90% of CO, HC, NOx and PM [1]. Meanwhile, in 2021, China's crude oil imports will be 512.978 million tonnes, down 5.4% year-on-year from 2020, the first decline since 2002, but oil dependency will still reach 72%.

Energy supply and environmental protection issues have come to the fore, and it is urgent to find suitable alternative fuels for vehicles, both from the perspective of ensuring energy security and environmental protection[2]. Methanol is a promising alternative fuel with wide production resources, mature technology and clean combustion. Current national standards are incorporating non-conventional pollutant emissions from new fuel vehicles, such as formaldehyde emissions from methanol-fuelled vehicles into regulation, but continuous measurement methods and equipment for formaldehyde are still being explored. This paper provides a basis for the next stage of formaldehyde emission testing and

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regulation of alcohol-based motor vehicles based on research and analysis of formaldehyde testing technology, domestic and international formaldehyde testing standards and measurement methods.

2 Domestic and international methanol vehicle policy standards

2.1 Foreign methanol vehicles and their development status

The first international conference on alcohol fuels was held in Sweden in 1976 to promote the development of alcohol fuels (mainly methanol and ethanol)\(^\text{[3]}\). Although the price of oil fell in the 1980s, the emphasis on environmental protection of the atmosphere led many countries to develop methanol as a clean alternative fuel for cars. Since 1980, Sweden has been introducing M15 methanol as an alternative fuel on a large scale, with plans to increase methanol substitution to one tenth of total gasoline and diesel consumption within ten years. The California Methanol Vehicle Demonstration Project, run by the CARB between 1978 and 1998, is the world's largest methanol vehicle demonstration project. The project has been running demonstrations of methanol vehicles since the late 1970s. In Japan, the "Special Committee on Methanol Fuel for Automobiles" was established in 1984; and the Methanol Fuel and Vehicle Trial Operation Programme was carried out from 1980 to 1994 \(^\text{[4]}\).

To encourage the development of alternative fuels and improve the atmosphere, the US Congress passed three legislative acts in five years: in 1988, President Reagan signed the Alternative Motor Fuels Act; in 1990, President Bush Sr. signed the Clean Air Act Amendments; and in 1992, he signed the Energy Policy Act \(^\text{[5]}\). Its main elements were: tax breaks for the production of clean alternative fuel vehicles and the use of alternative fuels; a requirement for cities to implement projects to clean up their urban environments; and government departments to take the lead in using methanol vehicles. These bills all promoted the development of methanol fuel in terms of policy and funding\(^\text{[3]}\). In the late 1990s, the use of methanol-fuelled vehicles in the US gradually went into decline. On the one hand, the cost advantage of methanol was weakened by the sharp fall in oil prices, and after the expiry of the 10-year cooperation agreement signed between several major oil companies such as Esso and Mobil and the US government, most of the original methanol filling stations were switched back to filling with gasoline. On the other hand, major agricultural countries such as Brazil and the United States have shifted to the development of zero carbon emission biomass ethanol fuel, resulting in the methanol fuel market being rapidly replaced by biomass ethanol. However, environmental pressures and a heightened awareness of the greenhouse effect have led to a renewed interest in the use of methanol as an alternative fuel. Iceland's Carbon Cycle International uses renewable energy and carbon dioxide to synthesize methanol, and it entered into a partnership with Geely Automobile Group in 2016 to test run Geely methanol cars on Icelandic roads. As an example, California formaldehyde testing standards:

(1) California Formaldehyde Testing Standards for Light Duty Vehicles

The US federal emission standards were the first to set formaldehyde emission limits for light-duty vehicles, and the California emission standards are based on the federal emission standards and will be phased in over the period 2015-2025.

Table 1. California LEV III Emission Limits (Passenger Cars or Light Duty Trains \(\leq 8,500\) lbs).

<table>
<thead>
<tr>
<th>Durability Category</th>
<th>NMOG+N\text{NO}_x (\text{g/mi})</th>
<th>CO (\text{g/mi})</th>
<th>Formaldehyde (\text{g/mi})</th>
<th>Particulate matter (\text{g/mi})</th>
</tr>
</thead>
</table>
(2) California Heavy Duty Vehicle Formaldehyde Testing Standards
The California Environmental Protection Agency (CARB) emission standards for heavy-duty engines and vehicles also set corresponding formaldehyde emission limits, which are shown in Table 3 below for 2004 and subsequent years.

Table 2. Emission limits for medium and heavy duty vehicles (g/bhp.hr).

<table>
<thead>
<tr>
<th>Model year</th>
<th>Emission category</th>
<th>NMOG+N Ox</th>
<th>NMOG</th>
<th>NOx</th>
<th>CO</th>
<th>HCHO</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td>2004</td>
<td>ULEV</td>
<td>2.4 or 2.5 and 0.5 NMHC cap</td>
<td>–</td>
<td>14.4</td>
<td>0.05</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLEV</td>
<td>2.0</td>
<td>–</td>
<td>7.2</td>
<td>0.025</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>2005-2007 6</td>
<td>ULEV</td>
<td>1.0</td>
<td>–</td>
<td>14.4</td>
<td>0.05</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLEV</td>
<td>0.5</td>
<td>–</td>
<td>7.2</td>
<td>0.025</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>2008-7</td>
<td>ULEV</td>
<td>–</td>
<td>0.14</td>
<td>14.4</td>
<td>0.010</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLEV</td>
<td>–</td>
<td>0.07</td>
<td>7.2</td>
<td>0.005</td>
<td>0.005</td>
<td></td>
</tr>
</tbody>
</table>

(3) Test methods for formaldehyde
The EPA standard specifies an FTP 75 cycle for formaldehyde emission testing cycles for light duty vehicles. In accordance with PART 86, a volume of diluted exhaust gas is drawn up in the diluted exhaust gas with a constant volume sampling pump while the cold start test is carried out. The diluted exhaust is passed through a two-stage DNPH solution in series to absorb the formaldehyde in the diluted exhaust and, at the end of the experiment, the formaldehyde concentration in the DNPH solution is analysed using a chromatographic analyser to further calculate the formaldehyde emissions.
2.2 National policy and regulations on methanol vehicles and fuels in China

2.2.1 Methanol vehicles and fuel policy development in China

In 2004, the National Development and Reform Commission issued two policies, "Policy on the Development of Automotive Industry" and "National Major Industrial Technology Development Special Project", which clearly pointed out that the state supported the development of methanol vehicles at the industrial development level, and methanol fuel was also listed as an important technical special project, defining the development position of methanol vehicles and fuel. In 2009, the Standardization Administration issued "Methanol for Automotive Fuel" and "Methanol Gasoline for Automotive Use (M85)". The two standards clarify the relevant production requirements, but for the comprehensive promotion of methanol fuel production and application, the current national standards for methanol fuel are still not sound, such as the methanol M15 and M100 national fuel standards with strong market appeal have been in the pipeline for a long time but are difficult to introduce. If these two standards are not accelerated, it will be difficult to realize Chinese methanol vehicle industry development strategy of "two highs and one low" (high ratio methanol fuels M85 and M100, low ratio methanol fuel M15). In 2012, the Ministry of Industry and Information Technology of the People’s Republic of China issued the Notice on the Pilot Work of Methanol Vehicles. In 2013, the State Council of the PRC issued “the Opinions on Strengthening Energy Saving and Emission Reduction in the Internal Combustion Engine Industry”, which emphasized the focus on accelerating the diversification of alternative fuels for internal combustion engines, of which methanol fuel and engines were listed as one of the important alternative fuels. In 2015 the Ministry of Industry and Information Technology of the People’s Republic of China issued “the Specifications for the Construction of Methanol Fuel Filling Stations for Vehicles” and “the Safety Specifications for the Operation of Methanol Fuel for Vehicles” to further standardize the operation of methanol fuel filling stations. In 2020, the Ministry of Ecology and Environment of the People’s Republic of China issued “the Measurement Method for Non-conventional Pollutant Emissions from Methanol-fuelled Vehicles”, which stipulates the measurement methods for formaldehyde and methanol in the exhaust gas of methanol-fuelled light-duty vehicles, heavy-duty engines and vehicles (including diesel/methanol dual-fuel engines and vehicles), and methanol in the exhaust of methanol-fuelled light-duty vehicles, heavy-duty engines and automobiles (including diesel/methanol dual-fuel engines and automobiles). The standard specifies a method for the analysis of formaldehyde in the exhaust of methanol-fuelled vehicles and heavy-duty engines, using high performance liquid chromatography.

2.2.2 Current situation of the development and application of methanol vehicles in China

Compared to electric vehicles, methanol vehicles and fuels still have not received focused national attention, and it is difficult for national policy funding and policy effects to be universally beneficial to the methanol vehicle industry, which is still a gap compared to the funding policy support during the methanol vehicle pilot demonstration abroad. In terms of local policies, the demonstration scale in Shanxi and Shaanxi provinces is large, and the provincial governments have given strong support in terms of fiscal policies, funding subsidies, license issuance, fuel refilling, land concessions and priority government procurement, etc. Shanxi province has also invested more in media publicity and public guidance, establishment of a methanol fuel price mechanism, and focus on infrastructure construction and ease of use [6].
Geely Automobile Group started to develop methanol-fuelled vehicles in 2005, and has become the only company in China to obtain the national product announcement for methanol vehicles. More than 1,000 Geely methanol cars have been launched in pilot areas such as Guiyang, Shanxi, Shaanxi, Gansu and Shanghai, with a maximum mileage of over 300,000 km. Geely is also planning the launch of private cars, and is expected to start the launch of private cars in Xi'an on a trial basis. It is understood that Great Wall Motors is also planning the technical development of methanol vehicles.

In terms of heavy-duty vehicles, five commercial vehicles equipped with diesel/methanol combination combustion engines also participated in the pilot project of methanol vehicles carried out by the Ministry of Industry and Information Technology of the People’s Republic of China in 2012 and have been in operation in the Yulin area of Shaanxi Province for more than two years. Since the completion of the first diesel/methanol dual fuel conversion vehicle in Shanxi, China in 2006, the diesel/methanol combination combustion technology has now been applied to over 100 heavy-duty vehicles in 14 provinces and cities across China. Feedback from users shows that heavy-duty diesel vehicles using the combined diesel/methanol combustion technology can achieve an average methanol replacement rate of over 30%, and the amount of methanol used to replace the equivalent volume of diesel is over 30% lower than the theoretical value, saving users over 15% in fuel costs each year. In addition, the application of this technology can meet the requirements of the National V emission regulations without the need for urea assistance, which not only reduces carbon smoke by more than 50% and NOx by 77%, but also eliminates the need for urea. This has greatly increased the initiative and motivation of users to use the technology, allowing them to actively participate in the energy saving and emission reduction initiatives. The large-scale application of combined diesel/methanol combustion technology will have a positive effect on reducing China's oil dependency and reducing emissions from heavy-duty diesel vehicles.

3 Research on formaldehyde testing methods

3.1 Spectrophotometric methods

Formaldehyde is detected by spectrophotometric, chromatographic and spectroscopic methods, depending on the nature of the instrument used.

(1) Acetylacetone spectrophotometric method

The acetylacetone spectrophotometric method is the method for the determination of formaldehyde specified in the standard GB/T 15516-1995 "Method for the determination of formaldehyde in air quality". The determination principle is that formaldehyde gas is absorbed by water and then reacts rapidly with acetylacetone in a solution of ammonium acetate with a PH value equal to 6 under boiling water bath conditions to produce a stable yellow compound, which is measured at a wavelength of 413nm [7]. It is characterised by simplicity of operation, good stability, low error and is free from interference from acetaldehyde when determining formaldehyde. However, the presence of SO2 and NOX in the air can have an effect on the results.

(2) Discolouring acid method

The colour change acid method is based on the reaction of a concentrated sulphuric acid solution of formaldehyde with a colour change acid to form a purple compound, which is stable for at least 16 hours and can be used to quantify formaldehyde by colourimetric analysis [8]. However, the reaction is slow and takes 20-30 minutes to complete, even in a boiling water bath.

(3) Phenol reagent spectrophotometric method
The phenol reagent spectrophotometric method is one of the detection methods specified in the standard GB/T 18204.26-2000 "Determination of formaldehyde in public places air", which is also used for quantitative analysis by colorimetric method. This method is characterised by simplicity of operation and high sensitivity, but the detection results are susceptible to interference by other aldehydes and SO₂.

### 3.2 Chromatography

(1) Gas chromatography

Gas chromatography is also one of the detection methods specified in the standard GB/T 18204.26-2000 "Determination of formaldehyde in public places air". The principle of detection is: formaldehyde is adsorbed on 6201 stretcher (coated with 2,4-DNPH) in an acidic environment; then carbon disulfide is applied to elute the process to produce formaldehyde hydrazone; then after the column, the measured sample is separated and determined by FID detector, retention time qualitative analysis and peak height quantitative analysis[8]. The gas chromatographic method is capable of simultaneous determination of formaldehyde, acetaldehyde and propionaldehyde and is not affected by SO₂ and NOₓ.

(2) High performance liquid chromatography (HPLC) method

The principle of detection by high performance liquid chromatography (HPLC) is basically the same as that of gas chromatography, with the difference that high pressure liquid chromatography is used for separation and the detector is of the UV absorption type.

### 3.3 Spectroscopy

(1) Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR detector detects the intensity of infrared radiation from exhaust systems and identifies different molecular structures in addition to the gas concentration.

(2) Proton transfer reaction-mass spectrometry (PTR-MS) method

The PTR-MS method is an on-line technique for the trace detection of VOCs, characterised by high sensitivity, fast detection and real-time availability.

A comparison of the advantages and disadvantages of the three formaldehyde testing methods mentioned above is shown in Table 3 below.

<table>
<thead>
<tr>
<th></th>
<th>Spectrophotometry</th>
<th>Chromatographic analysis</th>
<th>Spectroscopic analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advantages</strong></td>
<td>Easy to operate and low cost</td>
<td>Sensitive, accurate, reliable and less susceptible to interference</td>
<td>High sensitivity, short detection times and the ability to perform real-time on-line analysis</td>
</tr>
<tr>
<td><strong>Disadvantages</strong></td>
<td>Low sensitivity and long response time</td>
<td>Expensive equipment, costly to use and cumbersome to operate</td>
<td>Higher costs and more demanding experimental conditions</td>
</tr>
</tbody>
</table>

In addition to the above detection methods, formaldehyde detection methods are also oscillometric polarimetry, electrochemical sensor method, etc. Electrochemical methods have good prospects, but to overcome the selectivity, stability and other problems [9], how these methods are applied to real-time, continuous detection of automotive formaldehyde pollutant emissions still needs further research.
4 Study of methanol vehicle emission levels

4.1 Comparison of the main content of the I/M program

Wang Qi et al., Chang'an University, produced a formaldehyde emission tester based on the principle of phenol reagent spectrophotometry, proposed a calibration method for the equipment, and tested the formaldehyde emissions from complete vehicles in certain areas of Shaanxi. However, the formaldehyde tester still has certain problems: the existing tester does not address the influence of sulphur dioxide on the experimental results; the ambient temperature is low, and both the exhaust gas and the flow meter contain a large amount of water vapour and cannot be excluded, which affects the normal operation of the flow meter; and there are problems such as inconvenient installation and large errors [10]. Xie Yan et al. of South China University of Technology, developed an online formaldehyde detector to measure gaseous formaldehyde by Hantzsch reaction and absorbance photometry with an acquisition frequency of 1 Hz, which can accurately measure the HCHO concentration of gaseous pollutants with an HCHO absorption efficiency of 91.4% and a measurement range of 0~600 ppbv [11]. Zhang Fan et al. from Tsinghua University used high performance liquid chromatography (HPLC), gas chromatography-mass spectrometry (GC-MS) and Fourier transform infrared spectrometry (FT-IR) to measure the non-conventional pollutant emission pollutants from methanol engines. The results showed that both the Fourier transform infrared spectrometer transient value integration and the bag-pick chemical analysis were able to measure the emissions of formaldehyde, benzene and toluene in the vehicle exhaust relatively accurately, proving that the FITR method can measure the non-conventional emissions in the vehicle exhaust relatively accurately [12].

As there is currently no testing equipment available in the laboratory for direct formaldehyde measurements, this paper proposes to use a high performance liquid phase analyser to test formaldehyde in light duty methanol vehicles at different emission stages. Each test was repeated twice for the comparison of gaseous conventional pollutant and formaldehyde emissions from two methanol vehicles meeting the National V emission standard when burning gasoline and methanol respectively. Gaseous conventional pollutant and formaldehyde emissions from new and in-use vehicles equipped with National V methanol were also quantified. The main components of the high performance liquid chromatograph (HPLC) used included a vacuum degasser, automatic sample feeder, quadrupole pump, column oven and variable wavelength UV detector with a deuterium arc discharge lamp emitting UV light in the range of 190 nm to 600 nm. The results of the vehicle formaldehyde emission tests are shown in Figure 1 below.

![Fig. 1. Endurance test results of methanol vehicles meeting CN V emission standards.](image-url)
As can be seen from Figure 1, the new National V vehicles emit nearly one-third less CO and THC and nearly two-thirds less PM when running on methanol than when running on gasoline, but the NOx emissions are increased by 10.9%. Meanwhile, after a certain mileage of the vehicle (160,000 km), the emissions of all pollutants from the National V methanol test vehicle increased to varying degrees, with CO and THC emissions increasing by 23% to 30%, and NOx and formaldehyde emissions increasing very significantly year-on-year, reaching approximately 126% and 88% respectively.

![Fig. 2. Endurance test results of methanol vehicles meeting CN V emission standards.](image)

Figure shows the durability test results of a methanol vehicle meeting the National V emission standard. The results show that all conventional gaseous pollutant emissions are able to meet the requirements of the National V emission standard over the full life cycle of the vehicle.

On its own, methanol fuel does not have a low-carbon emission reduction function, but if methanol is produced through solar or wind power, which is the more popular term at present, "liquid sunshine methanol", then low-carbon emission reduction can be achieved.

5 Conclusion

This paper, based on research on methanol vehicles in China and abroad, has come to the following conclusions:

(1) Emissions: CO and THC emissions of methanol vehicles are lower than those of gasoline vehicles, NOx emissions are roughly the same as those of gasoline vehicles, and PM emissions are significantly lower; formaldehyde emissions are higher than those of gasoline vehicles.

(2) And as vehicle mileage increases, formaldehyde and NOx emissions from in-use methanol vehicles increase to a greater extent, but particulate emissions decrease significantly.

(3) The formaldehyde test method used in the existing formaldehyde standard is only for the new model type test and cannot achieve direct and continuous testing of formaldehyde. There is an urgent need to develop a direct formaldehyde measurement method for in-use methanol-fuelled vehicles and develop corresponding testing equipment.

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