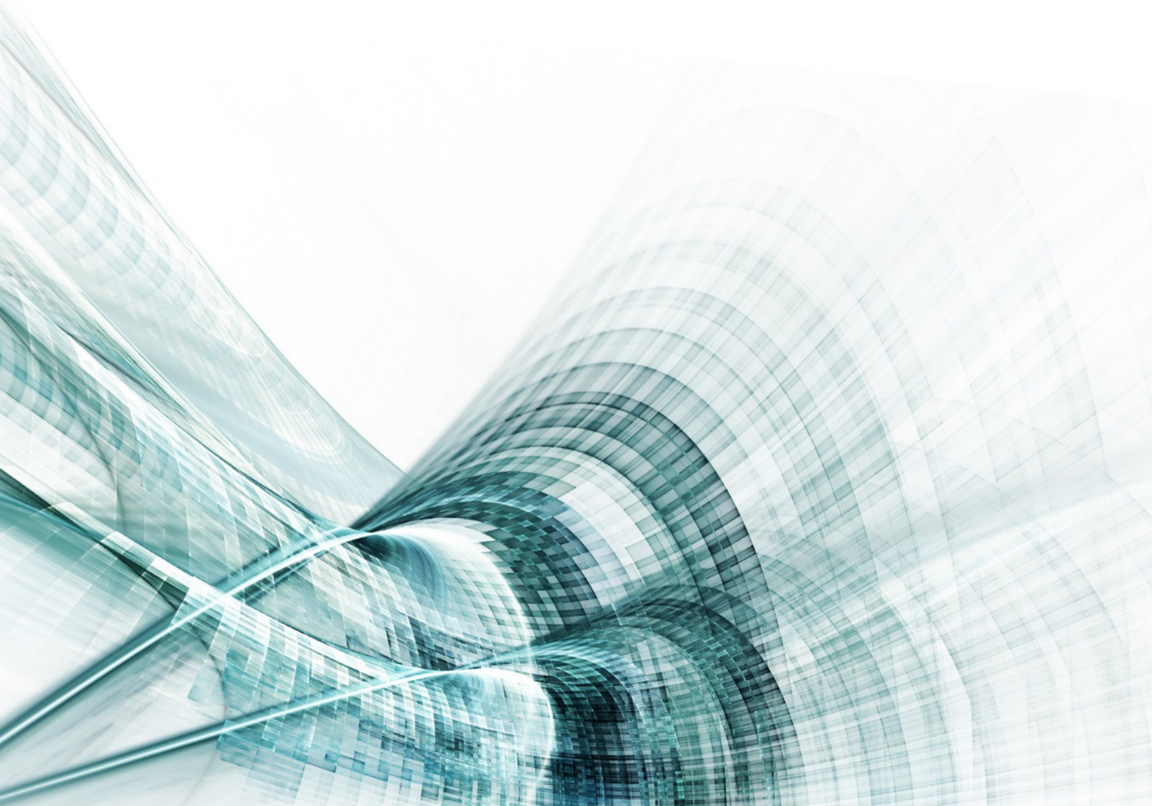
Annex 44

A Report from the IEA Advanced Motor Fuels Technology Collaboration Programme

Research on Unregulated Pollutants from Alcohol-Fuelled Vehicles

Zhang Fan and Tian Donglian
CATARC



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October 2016

Acknowledgements

The IEA-AMF Organization is grateful to the following countries and their representatives for their support in providing research to develop this report:

- Finland – Päivi Aakko-Saksa, Timo Murtonen, Piritta Roslund, Päivi Koponen and Jukka Nuottimäki, VTT; Panu Karjalainen, Topi Rönkkö, TUT; Hilkka Timonen, Sanna Saarikoski, Risto Hillamo, FMI;
- Canada – Jill Hendren and Debbie Rosenblatt (Environment and Climate Change Canada) and Natural Resources Canada (PERD) and Transport Canada (eTV);
- China – Zhang Fan and Tian Donglian (China Automotive Technology & Research Center);
- Sweden —Peter Ahlvik and Lars Eriksson (Ecotraffic on contract from the Swedish Transport Administration);
- Israel –Gideon Goldwine (Technion), Eran Sher (Technion), JRC VELA lab staff, Dr. Bracha Halaf (Ministry of Energy and Water Resources);

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Chapter 1 Introduction

1.1 Project background

The gradual depletion of petroleum resources throughout the world generates an increased urgency to develop alternative energy sources. Alcohol fuels have the advantages of a wide range of sources. These fuels can be manufactured from biomass raw materials, agricultural raw materials (e.g., sugar cane, cereals, and rice), timber and urban waste, and fossil fuels (e.g., natural gas, petrochemical, and coal). A number of countries support the use of alcohol alternative fuels. For example, the United States, Brazil, and Sweden encourage the use of ethanol fuel made from biomass materials. In addition, several regions in China, including Shanxi Province and Shanghai, have initiated a pilot program to promote the use of methanol fuel (Shangxi Province, 2005).

Due to the reduction of the limits of regulated pollutant emissions, unregulated pollutant emissions in the vehicle exhaust have attracted an increasing attention. Studies indicate that the use of alcohol fuels blended with gasoline in vehicles can reduce engine-out hydrocarbon (HC) and carbon monoxide (CO) emissions to some extent. The reduction occurs because the oxygen content in the fuel can promote the complete combustion of the fuel. However, more unregulated pollutants may be emitted, such as polycyclic aromatic hydrocarbons, aldehydes, and ketones (Charalampos et al. 2003, Hasan 2003, Vaughan et al 1994, Knapp et al. 1998, Poulopoulos et al. 2001). These substances have very strong stimulation and sensitization. They also have potential genetic toxicity and carcinogenic activity, which could significantly impact human health. Such as formaldehyde and acetaldehyde, they are easily converted into other secondary air pollutants because of its short atmospheric residence time. They are considered as nerve poisons, and even carcinogens, which cause serious damage to the health of the body because they stimulate people’s skin, eyes and olfactory mucous membrane. Inhalation or contacting a large number of benzene into the body can cause acute or chronic benzene poisoning. Mild poisoning can cause giddy, headache, nausea, chest tightness, weakness and confusion. Severe poisoning can cause coma which lead to death of respiratory and circulatory failure. Benzene is a strong carcinogen, which inhibits the body's hematopoietic function and reduces red blood cells, white blood cells and platelets (Yan et al. 2004).

The harm to human health from the aromatic hydrocarbon, aldehyde, ketone and other gas pollutants cannot be ignored. America established more stringent emission standards in the “Clean Air Amendments” (1990), formulated the new standards to control over 189 species of toxic pollutants, and classified 9 kinds of aldehydes and ketones (including formaldehyde, acetaldehyde, propyl aldehyde, acrolein, etc.) and 19 kinds of monocyclic and polycyclic aromatic hydrocarbons (including benzene, toluene, ethyl benzene, etc.) as hazardous emissions (Rutten et al. 1998). Japan promulgated “the emission prevention law” and classified 234 species of harmful air pollutants. 22 species of these were defined as priority pollutants, including benzene, toluene, acetaldehyde, etc. Britain, France, Germany and other European countries control the harmful pollutants such as benzene, polycyclic aromatic hydrocarbons according to promulgating and implementing a series of laws like “European air quality guidelines” and “Instructions on European air quality and cleaner air”. In China, the standards of environmental quality and emissions contain the strict rule about formaldehyde, benzene and total volatile organic compounds.

The issue of unregulated emissions has become an important factor that could hinder further development of alcohol alternative fuels. Therefore, it is necessary to investigate the unregulated pollutant emissions from vehicles fueled with alcohol alternative fuels. This type of research would serve to promote the application of alcohol alternative fuels in a more expedient manner.

By measuring the unregulated pollutant emissions of vehicles fueled with alcohol fuels, the main purpose of this project is to obtain the unregulated pollutant emission levels of alcohol-fueled vehicles and to gradually establish the measurement methods and limits of unregulated pollutant emissions.

Furthermore, our research will examine the influences that measurement methods, automotive technology, alcohol content in the fuel, ambient temperature, test cycles, and other relevant factors have on the vehicle unregulated pollutant emissions.

1.2 Main research content and report structure

The main activities of this project include:

(1) Literature survey, to obtain the existing measurement methods and test data of unregulated emissions from alcohol- fuelled vehicles;

(2) Comparative analysis of different measurement methods of unregulated pollutant emissions (such as FTIR, HPLC, GC and MS), to establish the complete measurement specifications;

(3) Research on effects of different vehicles (PFI, GDI) on unregulated pollutant emissions;

(4) Research on influences of alcohol content in the fuel (methanol 15%, 30%, 85% and ethanol 10%, 20%, 85%) on unregulated pollutants types and concentration values in vehicle exhaust emissions;

(5) Research on effects of the ambient temperature (25℃, -7℃) on the concentration of unregulated pollutant emissions;

(6) Investigation on the levels of unregulated pollutant emissions from alcohols fuelled vehicles in different test cycles (U.S. FTP75, Europe NEDC);

(7) Measurement on the regulated and unregulated evaporative pollutant emissions from vehicles fuelled with alcohols.

This report is the summary of above-mentioned research project. The structure of the report is shown as below:

Chapter 1 is Introduction, including project background, research content and project structure.

Chapter 2 is Literature survey, including unregulated emissions characteristics, measurement methods and previous research on emissions of alcohol fuelled vehicles.

Chapter 3 mainly introduces the light-duty vehicles emissions tests on the chassis dynamometer of Canada, Finland, China and Israel, including: test fuels, vehicles, main test equipment, test curves, regulated and unregulated pollutants analysis methods and other relevant information.

Chapter 4 compares instantaneous emissions of CO, CO2, and NOX pollutants as well as cycle average emissions of CO, CO2, NOX, formaldehyde, acetaldehyde, benzene, and toluene pollutants, in order to verify the accuracy and consistency of the various measurement methods.

Chapter 5 mainly introduces the emissions tests of alcohol fueled vehicles on the chassis dynamometer at normal and low temperatures and researches the influences of key factors on the vehicle emissions performance. It mainly contains the influences of alcohol content in the fuels on regulated and unregulated pollutants emissions from light-duty vehicles at normal and low temperatures, the influences of ambient temperature on vehicle pollutants emissions, and the influences of engine types on vehicle regulated emissions, unregulated emission and particulate emissions.

Chapter 6 mainly introduces the comparison emissions tests of the same light-duty vehicle fuelled with E10 fuel during European, American and Japanese emissions regulations on a chassis dynamometer, and researches the influences of different driving cycles on the regulated and unregulated emissions.

Chapter 7 is the conclusion and summary of the research carried out by Canada, Finland, China and Israel.

Chapter 2 Literature Review of Unregulated Pollutants Emissions

This chapter is the summary of literature survey, including unregulated emissions characteristics, measurement methods and previous research on emissions of alcohol fuelled vehicles.

2.1 Pollutants characteristics from vehicle exhaust emissions

There are many different kinds of vehicle exhaust emissions, aldehydes, ketones and aromatic hydrocarbons, etc. which catch the most attention from the researchers.

2.1.1 Aldehydes

Aldehydes is the compound combined with aldehyde group (-CHO) and alkyl (or hydrogen atoms). Aldehyde group consists of a carbon atom, a hydrogen atom and a double bond oxygen atom. Aldehydes in vehicle exhaust emissions generally include formaldehyde, acetaldehyde, acrolein, propionaldehyde, 2-butene aldehyde, methyl acrolein, butyraldehyde, benzaldehyde, amyl aldehyde and hexanal, etc. Totally formaldehyde and acetaldehyde are two of the main vehicle exhausts emissions in the aldehyde pollutants, accounting for about 70%-90% of the total aldehydes emissions (Sergio et al. 2007). In general, aldehyde pollutants are all toxic substances. It can not only result in the unwell symptom such as headaches, tiredness, cross-eyed and upper respiratory tract stimulation, but also in the case of acute poisoning cause the phenomenon of loss of consciousness and the vomiting. It is even more important that they show a certain genetic toxicity, as the compound belongs to direct electrophilic class.

Table 2.1 lists the main characteristic of aldehyde pollutants parameters. Seen from the table, expect for formaldehyde and acetaldehyde appearing gaseous at normal temperature, aliphatic aldehydes below C12 are liquids. The comparison of LD50 and MAC data shows that the most toxic pollutants are acrolein, methyl acrolein, 2-butene aldehyde and formaldehyde.

Formaldehyde is one of the most important pollutants in vehicle exhaust emissions. Formaldehyde is the next highest in the priority controlled list of toxic chemicals in China. It has been confirmed by the world health organization (WHO) as the carcinogenic substances and the material causing deformity. It is regarded as the source of allergy and also one of highly potential mutagenic material.

Acetaldehyde is another important pollutant in vehicle exhaust emissions. Toxicity of acetaldehyde is slightly less than that of formaldehyde, and as 83 times of ethanol. It has strongly excitant, which can stimulate the nervous centralis of vomit to make the person produce nausea, vomiting, cause the headaches because of brain shrinkage, and stimulate person’s peripheral nerve and skin.

2.1.2 Ketones

Ketones are the compounds constituted by carbonyl and two hydroxyls. Carbonyl group is the bivalent group made up of a carbon atom and a double bond of the oxygen atom group. Ketones in vehicle exhaust emissions generally includes acetone, 2-butanone, 2,3-butyl ketone, 2-pentanone, cyclohexanone, etc.

Table 2.1 the main characteristic parameters of aldehyde pollutants

Pollutants	molecular formula	molecular weight	oxygen content（%）	relative density（water=1）	boiling point（℃）	fusion point（℃）	LD50（mg/kg）	MAC（mg/m^3）
formaldehyde	CH_2O	30	53.3	0.82	-19.4	-92	800	3
acetaldehyde	C_2H_4O	44	36.4	0.788	21	-123	1930	Unspecified
acrolein	C_3H_4O	56	28.6	0.84	52.5	-87.7	46	0.3
propionaldehyde	C_3H_6O	58	27.6	0.8	48	-81	1410	Unspecified
2-crotonaldehyde	C_4H_6O	70	22.9	0.85	104	-76	240	Unspecified
methyl acrolein	C_4H_6O	70	22.9	0.85	69	-81	111	Unspecified
butyraldehyde	C_4H_8O	72	22.2	0.8	75.7	-100	5900	10
benzaldehyde	C_7H_8O	106	15.1	1.04	179	-26	1300	Unspecified
amylaldehyde	$C_5H_{10}O$	86	18.6	0.81	103	-91.1	3200	Unspecified
hexanal	$C_6H_{12}O$	100	16	0.83	128.7	-56.3	4890	Unspecified

Table 2.2 lists the main characteristic parameters of ketone pollutants. From the table, the boiling point of ketones is higher than 50℃ and the melting point is lower than 40℃. Thus, the ketones are liquid at room temperature. The main impacts of ketones are anesthesia and inhibitor on the nervous centralis system. Through the contrast of the LD50 and MAC data, it can be seen that the toxicity of ketones is lower than that of aldehyde.

Acetone is the largest ketones in vehicle exhaust emissions, which belong to the slight nervous centralis inhibitors. Contacting high concentrations emissions may cause damage of liver, kidney and pancreas for individuals. Long-term damage from acetone to the human body is shown as the stimulus symptoms to eyes, such as lacrimation, photophobia and corneal epithelium infiltrating, and also appears dizziness, burning sensation, throat irritation, coughing, etc.

2.1.3 Aromatic hydrocarbons

Aromatic hydrocarbons are hydrocarbons which contain one or several benzene ring structures in the molecule. According to the number and the connection mode of benzene rings, aromatic hydrocarbons can be divided into monocyclic aromatics hydrocarbons and polycyclic aromatic hydrocarbons by the structure.

Monocyclic aromatic hydrocarbons are mainly benzene homologues, including benzene, toluene, ethylbenzene, o-xylene, m-xylene, p-xylene, etc. Table 2.3 shows the main characteristic parameters of monocyclic aromatic hydrocarbon pollutants.

Table 2.2 The main characteristic parameters of ketone emission

Pollutants	molecular formula	molecular weight	oxygen content（%）	relative density（water=1）	boiling point（℃）	fusion point（℃）	LD50（mg/kg）	MAC（mg/m^3）
acetone	C_3H_6O	58	27.6	0.8	56.5	-94.6	5800	400
2-butanone	C_4H_8O	72	22.2	0.81	79.6	-85.9	3400	Unspecified
2, 3-butyl diketone	$C_4H_6O_2$	86	37.2	0.99	88	No data	1580	Unspecified
2-pentanone	$C_5H_{10}O$	86	18.6	0.81	102.3	-77.5	3700	Unspecified
cyclohexanone	$C_6H_{10}O$	98	16.3	0.95	115.6	-45	1535	50

Table 2.3 main characteristic parameters of monocyclic aromatic hydrocarbons pollutants

Pollutants	molecular formula	molecular weight	relative density（water=1）	boiling point（℃）	fusion point（℃）	LD50（mg/kg）	MAC（mg/m^3）
Benzene	C_6H_6	78	0.88	80.1	5.5	3306	40
Toluene	C_7H_8	92	0.87	110.6	-94.9	5000	100
Ethyl benzene	C_8H_{10}	106	0.87	136.2	-94.9	3500	50
o-xylene	C_8H_{10}	106	0.88	144.4	-25.5	1364	100
Meta-xylene	C_8H_{10}	106	0.86	139	-47.9	5000	100
paraxylene	C_8H_{10}	106	0.86	138.4	13.3	5000	100

The main part of aromatic hydrocarbons from vehicle exhaust emissions is benzene, toluene and xylene. Mononuclear aromatics are all toxic. Benzene has the strongest effect on the nervous centralis and blood. It is generally believed that benzene entering into body can form metabolites with blood toxicity in the hematopoietic tissue itself. Long-term exposure to benzene can cause genetic and bone marrow damage. The blood picture check presents white blood cells and thrombocytopenia reducing, pancytopenia, aplastic anemia, and even leukaemia.

2.2 Previous research on unregulated emissions in vehicle exhaust

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 (Wei et al. 2008, Liu et al. 2007, Charlotte et al 2010, Zhang et al. 2006, Zhang et al. 2008, Ge et al. 2008, Zhang et al. 2010, Liu et al. 2010, He et al 2003, Dong et al. 2006). For example, in Xi'an Jiaotong University, Tianjin University and Jilin University unburned methanol and formaldehyde emissions from methanol-gasoline engines were measured by GC. In Chrysler Motor Company, The American auto testing laboratory and Beijing Institute of Technology, HPLC and GC-MS were used to measure benzene and formaldehyde emissions during the driving cycle from methanol-gasoline vehicles. In Tsinghua University, methanol, formaldehyde and acetaldehyde emissions before and after the catalyst from methanol-gasoline engines were also measured by FTIR. In Xi'an Jiaotong University, Tsinghua University, Tianjin University and the Massachusetts Institute of Technology, GC was used to measure formaldehyde, acetaldehyde and ethanol emissions from ethanol-gasoline engines. In the French Institute of Petroleum, 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. A few of typical projects researching on the effects of alcohol proportions in fuels on vehicle pollutant emissions are discussed in the following sections.

2.2.1 Research on the effect of E85 on the exhaust emissions

High-oxygen-containing fuels, for example up to 85% ethanol (E85), can be used in special flexible-fuel vehicles (FFV). In Brazil, FFV cars are also designed for the use of hydrous E100 fuel. Methanol (M85) was used in the FFVs in early 90’s, and now it is used again, for example, in China. FFV cars are basically spark-ignition gasoline cars with some modifications. For example, all materials in the FFV cars are compatible with ethanol. Due to E85 fuel’s low energy content, fuel injectors of the FFV cars are designed for higher fuel flows than in conventional gasoline cars leading to higher volumetric fuel consumption despite of lower energy consumption. Feedback control in FFV cars adjusts fuel delivery and ignition timing. Ethanol's higher octane rating would enable an increased compression ratio to achieve better energy efficiency. However, FFV cars still represent a compromise when compared to dedicated alcohol cars. The ignition of ethanol is poor, and therefore excess fuel is injected during cold starts when using E85 fuel to achieve performance similar to gasoline cars. Consequently, some exhaust emissions tend to be high when using E85 in the cold-start when the three-way catalyst is not warmed-up. Engine- and emissions-control technologies are expected to reduce cold-start exhaust emissions of the FFV cars using the E85 fuel in the future. (Lupescu 2009, Chiba et al. 2010, Kabasin et al. 2009, Yanowitz and McCormick 2009). Recently, a concern of adverse effect of ethanol on the aged TWC catalyst has been presented (Winkler et al. 2013).

When the automotive exhaust emissions are evaluated, it is important to consider harmfulness of the emissions. The US EPA's Mobile Source Air Toxic (MSAT) list from 2007 discusses key MSATs: benzene, 1,3-butadiene, formaldehyde, acetaldehyde, acrolein, polycyclic organic matter (POM), naphthalene, diesel exhaust and gasoline particulate matter. Benzene, 1,3-butadiene, formaldehyde and benzo[a]pyrene have been classified as human carcinogens (IARC, 2010, 2012). Acetaldehyde (IARC, 1999) has been classified as a possible carcinogen. Many other compounds, such as PAHs and nitro-PAHs have been classified as proven, probable or possible carcinogens to humans. Ethene forms potential damages for plants and contribute in the formation of ozone and peroxylacetyl nitrate

(PAN) (Gaffney and Marley 2011). Risk factors for calculating the cancer potency of exhaust gas are defined by many organisations. OEHHA (2009) defines cancer unit risks and potency factors for 107 carcinogenic substances or groups of substances. The US EPA IRIS (Integrated Risk Information System) is a human health-assessment programme that evaluates quantitative and qualitative risk information for effects that may result from exposure to environmental contaminants. The Nordic Swan labelling criteria for biofuels define substances, which are measured in accordance with a particular protocol, and calculate the cancer potency of exhaust gas using risk factors (Nordic Ecolabelling 2008). There are differences in the risk factors defined by different organizations.

Volatile organic compounds (VOC) contribute to the formation of ground-level ozone together with nitrogen oxides (NO_X) in the presence of heat and sunlight. Potential interactions between ozone and particulate matter emissions have been suggested. Precursor gases emitted by transport sources affect PM2.5, PM10 and ozone formation locally and in other regions. Exhaust and evaporative emissions from gasoline cars are the dominant source of VOCs within the transport sector, contributing 19% to the total VOCs emitted in 2010. Ozone causes adverse health effects, for example irritation of the respiratory system, coughing, throat irritation, reduction of lung function and induced asthma. There is also evidence of the effect of ozone on, for example, cardiovascular related morbidity (US EPA 2007). Ozone contributes to damage to plants and ecosystems, which may lead to species shifts and losses reflecting also related goods and services (US EPA 2007). Individual VOC species contribute differently to formation of ozone and oxidants. Carter and Atkinson (1987) developed a maximum incremental reactivity (MIR) scale to assess the ozone-forming potential (OFP) of any emitted molecule. Environmental impacts can be analyzed by various methodologies, such as CML2001 or ReCiPe2008, which take into account OFP, but also acidification potential (AP), photochemical oxidation creation potential (POCP), particulate matter formation potential (PMFP) and marine eutrophication potential (MEP) (Querini et al. 2011).

Transformation of primary exhaust emissions into secondary products is an important aspect when transport sector's emissions are assessed. For example, about 30% of PM10 measured is in the form of secondary inorganic sulphate and nitrate aerosols, which are formed from the transformation of gaseous SO_2, NO_X and NH_3 emitted from various sources. These aerosols are presumably even more important as regards PM2.5 (EEA 2012a). Secondary organic aerosols are formed from atmospheric oxidation and subsequent condensation of various VOCs (EEA 2012a, AQEG 2005).

Ammonia originates mainly from agricultural sources. However, concern of traffic sources in the production of ammonium aerosols increased as the use of urea-based SCR systems for NO_X control for diesel vehicles became common. Ammonia is also formed by the three-way catalysts of the spark-ignited gasoline cars. Nitrous oxide (N_2O), a strong greenhouse gas, is also induced by catalyst chemistry under lean conditions. (Meija-Centeno 2007, EEA 2012b).

NO_X, CO and HC emissions tend to be lower or at the same level for E85/FFVs than for gasoline at normal test temperature. NO_X comprises almost totally of NO while NO_2 emissions are low. Despite of low CO and HC emissions at normal test temperature, at -7°C higher or similar emission level has been observed for E85 as for gasoline (Laurikko et al. 2013, Aakko et al. 2011, Yanowitz and McCormick 2009, Graham et al. 2008, Westerholm et al. 2008, De Serves 2005, Aakko and Nylund 2003). The latent heat of vaporization of ethanol is higher than that of gasoline leading to poor cold-startability and high emissions of organic gases at cold starts. (Chiba et al. 2010). On the other hand, fuel evaporative emissions are lower for E85 than for gasoline (Yanowitz and McCormick 2009, Westerholm 2008). Lower permeation emissions have also been reported for the E85 fuel than the non-ethanol fuel (Haskew and Liberty 2006, Kassel 2006, Stahl et al. 1992).

Higher methane and ethene, but lower benzene, toluene and 1,3-butadiene emissions are reported for E85 than for gasoline at normal temperature (Clairotte et al. 2013, Karavalakis et al. 2012, Yanowitz and McCormick 2009, Westerholm et al. 2008). At -7°C, high methane, ethene, acetylene and BTEX emissions have been observed for the FFV car using the E85 fuel. (Aakko-Saksa et al. 2011).

The formaldehyde, acetaldehyde and ethanol emissions tend to increase substantially when E85 is compared with gasoline at cold starts at low temperatures (Clairotte 2013, Karavalakis et al. 2012, Aakko-Saksa et al. 2011, Yanowitz and McCormic 2009, Graham

2008, Westerholm et al. 2008 and De Serves 2005). Westerholm et al. (2008) reported that acetaldehyde emissions were 8–15 times higher for an FFV car using E85 than when using E5 at normal test temperature, and more than 100 times higher at a test temperature of -7°C. Acetaldehyde, formaldehyde, and ethanol emissions represent a major part of organic gas emissions with ethanol containing fuels during the engine cold start (Chiba et al. 2010). However, when engine and catalyst are warmed up, lower or similar acetaldehyde and ethanol emissions have been reported for E85 than for gasoline (De Serves 2005).

Millet et al. (2012) reported that the increased ethanol use is estimated to elevate acetaldehyde concentration in atmosphere, which leads to higher PAN: NO_X ratio via peroxylacetyl radicals combined with lower NO_X emissions.

Particulate matter (PM) emissions for FFVs using E85 have been lower than for gasoline at normal temperature (Yanowitz and McCormic 2009). At -7°C, higher PM emission has been observed for the E85 fuel than for gasoline, assumedly related to cold-start behavior of car (Westerholm et al. 2008). Hayes et al. (2013) observed that elemental carbon emissions decreased with increasing ethanol content of fuel (Hays et al. 2013). For E85, low PAH emissions have been reported at normal test temperature, but elevated PAH emissions and cancer potency at -7°C (Westerholm et al. 2008, Aakko-Saksa et al. 2011).

Lower particle number emissions have been observed for E85 than for gasoline at normal temperature, but the opposite has been seen at

-7°C (Westerholm et al. 2008, De Serves 2005). According to Lee et al. (2009), particle number emission decreased by 37% when E85 was compared with gasoline. In these studies, only dry particles were measured with so called "PMP" procedure. Szybist et al. (2011) concluded that low particle number emissions for E85 would enable using efficient direct-injection technology without penalty of high particle emissions.

Lower OFP for E85 has been reported when compared with gasoline at normal temperature (Graham et al. 2008). At cold temperature E85 may induce higher OFP due to increased ethanol, ethene and acetaldehyde emissions (Clairotte et al. 2013, Aakko-Saksa et al. 2011). These studies were not taken into account atmospheric chemistry or the NO_X emissions. In the US, E85 has been estimated to slightly increase ozone under summer, but particularly over winter conditions. (Jacobson 2007, Ginnebaugh and Jacobson 2012). Negligible changes or varying results in OFP and PM have been reported for the dedicated E85 vehicles in the U.S. (Nopmongcol et al. 2011, Alhajeri et al. 2012). Formation of ozone is a complex process involving CO, VOC, NO_X and meteorological conditions, and it is not straight-forward to conclude the impact of fuel. (Querini et al. 2011). Fridell et al. (2014) estimated that for regions in Sweden health risks decrease with E85 compared with gasoline due to decreased NO_X in relation to smaller effects on ozone, acetaldehyde, PM2.5 and benzene. However, authors pointed out that NO_X indicator may not be applicable for the E85 case, because there are differences in exhaust components associated with NO_X from different combustion processes.

Well-to-Wheel (WTW) environmental impacts of cars and fuels were analyzed by Querini et al. (2011). Differences in emission impacts between fuels (E85, gasoline) were less significant than between car generations from Euro 3 to Euro 5. Also in the scenarios by Winther et al. (2012) emission impacts of E85 on NO_X, VOC and CO were small. These conclusions were based on the car emissions at normal temperature. According to Huo et al. (2009), E85 reduces VOCs, NO_X, PM and CO emissions in the life-cycle perspective in urban areas by up to 30%, as the major part of emissions are released in production of ethanol. Yang et al. (2012) claim that E85 does not necessarily outperform gasoline when wide spectrum of life-cycle environmental impacts is considered.

Ammonia (NH_3) or nitrous oxide (N_2O) are not directly fuel-related emissions. However, fuel has some indirect influence on these catalyst-generated emissions. Mejia-Centeno (2007) observed that low sulphur fuels reduce the formation of nitrous oxide emission while favouring the formation of ammonia. Clairotte et al. (2013) reported of lower ammonia emissions for E85 than for E5. Graham et al. (2008) observed that N_2O tends to increase with increasing ethanol content of fuel. In one study, nitrous oxide emissions were very low, mostly below 4 ppm, for three spark-ignition cars representing different engine technologies regardless of fuel. (Aakko-Saksa 2011)

2.2.2 Research on the effect of low content methanol fuels

The INTROMET (INTroduction of METhanol) project. It was started in 2003 with financial support from the Swedish Energy Administration (Ecotraffic, 2006). The objective was to study the introduction of methanol as a motor fuel, primarily via low-level blending in gasoline. One car, a Renault Clio of model year 2002, was tested at several fuel blends. The tests were conducted at a chassis dynamometer at AVL MTC in Jordbro. To isolate the effect of methanol on emissions, the base gasoline was ethanol free, and blended with 0 (baseline), 5, 10, 15 and 20 % methanol. The test cycle was the NEDC driving cycle and double tests at each fuel was conducted. The test temperature was 22°C.

Besides regulated emissions, also aldehydes (formaldehyde and acetaldehyde), particle mass, particle number and particle size distribution were measured. The latter components were measured with an electrical low-pressure impactor (ELPI™ by Dekati in Tampere, Finland). The results for CO and HC emissions showed clear trends of decrease with higher content of methanol but in some cases, the measurement scatter was relatively large. The measurement scatter for NO_X emissions was relatively high but the comparatively high level at the highest blending level suggests that the air-fuel ratio could have been too lean. This is a well-known phenomenon and also indicates that the blending limit for this particular car could lie at ~15 %. Modal emissions show the two phases of the driving cycle and the total weighted result. Formaldehyde emissions showed an increasing trend while the acetaldehyde emissions were decreasing with increasing methanol content.

Interestingly, the particle mass (PM) emissions decreased substantially with increasing methanol content. The decrease from baseline condition (0 % methanol) to the level for 20 % methanol content was as high as approximately a factor of 5. Note that this was during test at normal ambient conditions, which was +22°C in this case. Therefore, it is not known if this very positive trend of PM vs. blending rate would also be valid at lower ambient temperatures. Extensive data on real-time emissions of particle number and size distribution were collected. One general observation was that significant levels of particles were emitted in the first acceleration with the cold engine and the acceleration in the highway part of the test cycle. The results for particle number and size distribution were not clear. Since the definition of solid particle number (SPN) was not conceived when these tests were carried out, it should be noted that the tests were not made with a sampling and dilution system that removes volatile particles. Thus, any firm conclusions from the results on particle number and size distribution should not be made. A trend towards a marginal reduction of the CO_2 emissions could be seen. Since the ratio between hydrogen and coal is higher in methanol than in gasoline, this could explain the results for fuel consumption and CO_2 emissions.

Emission tests on an engine dynamometer were carried out at the Chalmers Technical University in Gothenburg. The same fuel compositions as in the chassis dynamometer tests were used. Only regulated emission components were measured. A port-injected (Volvo) and a direct-injected engine (Mitsubishi) were used. Emissions were measured at various speed and load test points.

Methanol blending seems to have a certain positive impact on CO and energy efficiency. For HC and NO_X no clear impact could be seen. The trend was a small increase for HC for both engine types while NOX decreased for the port-injected engine but increased marginally for the direct-injected engine. The exhaust content of methane, acetaldehyde, formaldehyde and methanol in the exhaust was very low. The catalyst will reduce these levels even further with the exception for methane. In summary, it was concluded that no objections for blending methanol in gasoline could be found. Optimizing the engine and its injection system would give further improvements.

The Swedish M15 project in the 1970's and 1980's. In the search for alternate fuels for the transportation sector, methanol was considered a competitive candidate in the late 1970's. It was anticipated that methanol-gasoline blends may be used in the automobiles at that time with minor adjustments. In the process of evaluating the environmental implications when gasoline is replaced by a methanol-gasoline blend, comparative emission data have been generated.

During 1975 – 76 two fuels were tested at the BP laboratories in Sunbury on Thames for Volvo and Swedish companies involved in introducing methanol as a component in gasoline. The main interest was to check the increase of octane requirement for a special blend of

16 % methanol and 4 % isobutanol in a mixture of reformate and straight run gasoline. Octane requirement increased for a test period of 30 000 km and had not stabilized. One fuel pump and one carburettor float malfunctioned due to the fuel. Nothing was said about cleaning additives in the reference or test fuel. There was a tendency for higher increase of octane number requirement for vehicles run on the methanol containing fuel compared to references run on a reference gasoline without methanol (BP, 1976).

Four vehicles of 1976 model, two Volvo 244 cars equipped with carburettors and two Volvo 264 cars with fuel injection without catalysts, were used for tests with gasoline followed by tests with a methanol-gasoline blend. No attempt was made to optimize the engine systems for best utilization of the methanol, for example, compression ratios and ignition timing. When running on gasoline, the vehicles were adjusted according to the manufacturer´s specifications. When running on methanol-gasoline blend the carbon monoxide content in the exhaust gas was used as a measure of the "leaning out effect" caused by methanol, which was compensated for. No other adjustments were made. Drivability was considered satisfactory with both fuels. However, no specific drivability tests were made. Ordinary leaded gasoline and a methanol –gasoline blend consisting of 80 % (volume) of lead-free gasoline, 18 % methanol and 2 % isobutanol were used.

Tests were made on a chassis dynamometer according to the 1975 Federal Emission Test Procedure and also the European Test Procedure. Carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_X) sere measured and fuel consumption was calculated. In addition, total aldehydes, formaldehyde and polynuclear aromatic hydrocarbons (PAH) were analyzed.

The following conclusions were drawn from the study of four Volvo cars where a methanol-gasoline blend was substituted for a standard gasoline: CO, HC and NO_X tended to slightly decrease (provided that the carburettor and fuel injection system are carefully maintained). Total aldehydes increased, formaldehyde being responsible for most of the increase. The amount of PAH seems to depend more on the driving cycle and driving pattern prior to the test than on the fuel. No significant difference could be detected between the two regarding PAH emissions. The fuel consumption was about the same on an energy basis. With widespread use, adjustment of the fuel system will be a critical point. Monitoring the carbon monoxide content at idling will not be sufficient to obtain optimal performance.

The experimental program was conducted by the Swedish Methanol Development Co. (SMAB), the group for Exhaust Gas Research, AB Atomenergi and the department of Analytical Chemistry, Arrhenius Laboratory, and Stockholm University. The tests in the project were run in the last quarter of 1977. The test was performed on chassis dynamometer and regulated emissions measured according to best available technique of that time for example measuring after CVS system and HC measured with FID for all driving cycles (Britt-Marie Bertilsson et al., 1978-02-01).

Emissions were tested according to the old ECE test procedure with four consecutive city cycles with a maximum speed of 50 km/h. The

US-73 test cycle was composed of one Yht and one Ys cycle with maximum speeds around 90 and 55 km h (Bertilsson & Egebäck, 1978). The regulated emissions were very high, compared to what we demand today, but typical of well-maintained vehicles of that time. The two vehicles with carburettors had idle emissions of 3-4 % CO, the ones with fuel injection 1-2 %. The M20 has a leaning out effect on the emissions, especially the US cycles with their higher load. For the ECE tests, formaldehyde was 35 to 45 % higher and total aldehydes were 10 to 30 % higher for M20 compared to gasoline. For the US tests, formaldehyde was 15 to 35 % higher and total aldehydes were 10 to 30 % higher. The increase of total aldehyde values were almost all the result of increased formaldehyde emissions when running on M20.

Temperature in the exhaust system is very much dependent on developed power from the engine and during start-up phase losses occurs via condensation of water and the deposition of combustion products in pipes and mufflers. PAH emissions were sampled from undiluted exhaust with a constant flow system based on laminar flow elements in the engine air flow and after the sampling equipment. The volume sampled was about 7 % of the total flow. After cooling in all glass cooler, the gas was filtered in a 127 mm glass fibre filter 99.9 % effective on 0.3 µm particles. Acetone was used for rinsing the cooler after the test and added to the condensed water which was extracted and analyzed separately. Emissions of PAH were generally much higher in the US test cycles which could depend on the higher load and thus higher temperature rise and exhaust pipe/muffler temperature. This in turn will help to evaporate PAH from deposits in engine and exhaust system. Emissions of PAH were on average 25 % higher for the M20 fuel. The cold started cycles however (ECE cold and US-73), has higher relative PAH emissions for the M20 fuel, which could be explained by cold start enrichment washing the inlet system and the cylinder walls thus dissolving deposited PAH in engine and exhaust system.

Chapter 3 Test Matrix and Analysis Methods

This chapter mainly introduces the light-duty vehicles emissions tests on the chassis dynamometer of Canada, Finland, China and Israel, including: test fuels, vehicles, main test equipment, test curves, regulated and unregulated pollutants analysis methods and other relevant information.

3.1 Canada

Testing was conducted by Environment and Climate Change Canada’s Emissions Research and Measurement Section. This test program was supported by Transport Canada’s ecoTECHNOLOGY for Vehicles Program (eTV) and Natural Resources Canada’s Program of Energy Research and Development (PERD) Advanced Fuels and Technologies for Emissions Reduction (AFTER 9)

3.1.1 Test matrix

Two vehicles (shown in Table 3.1), a Ford Transit Connect employing port fuel injection (PFI) and a Ford Focus flexible fuel vehicle (FFV) with gasoline direct injection (GDI) were tested on 0% and 10% ethanol blended gasoline (E0 and E10). Three test cycles were used representing city driving and cold-start (FTP-75), aggressive high speed driving (US06), and free flow highway driving (HWFCT). Tests were performed at temperatures of 22°C, -7°C, and -18°C. The Ford Focus was also tested on two different 85% by volume ethanol blends (E85), summer (E85sum) and winter (E85win), while operated at 22°C, and -7°C and -18°C respectively. Table 3.2 provides a summary of the test matrix.

Table 3.3 lists the test fuel properties. The certification fuel was splash blended by volume with fuel grade ethanol to produce E10. The splash blending method was used for expediency and it is noted that the fuel chemistry of splash blended and tailor blended ethanol fuels is different.

Table 3.1 Test Vehicle Specifications

VEHICLE ID	GDI	PFI
MODEL YEAR	2012	2013
TRANS TYPE AND # OF GEARS	5-speed manual	4-speed automatic
GVWR (lbs)	3990	5005
TEST WEIGHT (lbs)	3250	3750
ENGINE	2.0L Ti-VCT Wall Guided Spark Ignition Direct Injection I4, 160HP	2.0L DOHC I4 PFI, 136HP
EMISSION STANDARD	Tier 2 Bin 4 LDV, LEV-II ULEV	Tier 2 Bin 4 LDT1
EMISSION CONTROL	TWC/HO2S/HAFS/DFI	TWC/HO2S/EGR/SFI

Table 3.2 Test Matrix and Number of Repeats

Vehicle	**Fuel**	**Temp. (°C)**	**FTP**	**US06**	**HWFCT**
TC2012-13 (PFI)	E0	22	5	8	4
		-7	2	-	-
		-18	3	-	-
	E10	22	2	3	3
		-7	3	-	-
		-18	4	-	-
TC2012-02 (GDI)	E0	22	5	5	5
		-7	3	-	-
		-18	3	-	-
	E10	22	2	3	3
		-18	3	-	-
	E85sum	22	3	3	3
	E85win	-7	2	-	-
		-18	4	-	-

Table 3.3 Test Fuel Properties

Fuel Identification	Method	E0	E10	E85sum	E85win
Carbon, % wt	ASTM D5291	86.31	82.40	57.60	59.49
Hydrogen, % wt	ASTM D5291	13.34	12.99	13.14	13.29
Density, kg/m^3 @ 15 ^{o}C	ASTM D4052	743.0	748.3	779.3	769.9
Oxygen, % wt		0	3.30	29.26	27.22
Specific Gravity °API	ASTM D4052	58.69	57.42	49.90	52.13
Specific Gravity 60/60F GRAV		0.744	0.749	0.780	0.771
Net Heating Value MJ/kg	ASTM D240 or ASTM	43.0	41.7	29.7	30.7
Reid vapour pressure kPa	ASTM D5191	62.7	68.7	45.0	78.0
Sulphur, ppm	ASTM 5453	29	32	6	8
Aromatics, % vol	ASTM D1319	28	29.4	N/A	N/A
Olefins, % vol		1	0.9	N/A	N/A
Saturates, % vol		71	69.7	N/A	N/A
Distillation , °C	ASTM D86				
10%		52.8	49.9	71.7	70.1
50%		106.1	100.4	77.5	77.2
90%		159.4	158.5	78.4	78.4
Ethanol % vol	ASTM D5501	0	9.8	82	75

3.1.2 Analysis Methods

Exhaust emissions were measured and characterized including, on all cycles, CO, NO_X, THC, TPM, and CO_2. On the FTP-75 and US06 cycles additional exhaust emission characterization included N_2O, CH_4, carbonyl compounds, and VOCs. Fuel consumption and NMOG were calculated based on measured emission rates. This summary report provides detailed results and analysis of CO, NO_X, THC, TPM, NMOG, CO_2, N_2O, CH_4, total carbonyl, acetaldehyde, formaldehyde, and acetone emission rates, as well as fuel consumption. Unburned ethanol was also analyzed over the FTP-75 E85 test condition. PM speciation including organic and elemental carbon (OC/EC) by the NIOSH 5040 method and particle number and size distribution was also conducted over select test modes. Table 3.4 summarizes the emissions characterization. Table 3.5 gives the emission analyses and methods.

Table 3.4 Emissions Characterization Matrix

Test Cycle	**Temp. (°C)**	**Regulated**	**GHG**	**Carbonyl**	**Ethanol (E85 only)**	**VOC**	**EEPS**	**OC/EC**
FTP-75	22	√	√	√	√	√	√	√
	-7	√	√	√	√	√	√	√
	-18	√	√	√	√	√	√	√
HWFCT	22	√	-	-	-	-	-	-
US06	22	√	√	-	-	-		

Table 3.5 Emission Analyses and Methods

Compound	**Analysis Method**	**Sample Collection**
Carbon Monoxide (CO)	Non-Dispersive Infrared Detection (NDIR)	Kynar™ Bag
Carbon Dioxide (CO_2)	Non-Dispersive Infrared Detection (NDIR)	Kynar™ Bag
Oxides of Nitrogen (NO_x)	Chemiluminescence Detection	Kynar™ Bag
Total Hydrocarbons (THC)	Flame Ionization Detection (FID)	Kynar™ Bag
Total Particulate Matter (TPM) 40 CFR86	Gravimetric Procedure Mettler Toledo MT-5	47 mm Teflon Filters
Ethanol	Innova 1412 Photoacoustic anlayser	Kynar™ Bag
Carbonyl Compounds (i.e. Formaldehyde, Acetaldehyde)	High Performance Liquid Chromatography	2,4-DNPH Coated-Silica Gel Cartridges

Methane (CH_4)	Gas Chromatography	Kynar™ Bag
Volatile Organic Compounds (VOC) (i.e. benzene, toluene)	Gas Chromatography – Flame Ionization Detection	Kynar™ Bag
Nitrous Oxide (N_2O)	Gas Chromatography with Electron Capture Detection	Kynar™ Bag
Organic Carbon and Elemental Carbon	Modified NIOSH 5040	Fired 47mm Quartz filters
Particle Size Number Distributions	TSI 3090 Engine Exhaust Particle Sizer (EEPS) with an ELA-111Dekati Thermodenuder	Continuous Dilute Exhaust
Fuel Consumption (FC)	Calculated based on Industry Standard Carbon Balance	

3.2 Finland

3.2.1 Test fuels and vehicles

Test fuels were comprised of a regular commercial E10 (max 10% ethanol), E85 (85% ethanol), and E100 (100% ethanol). E10 and E85 were available from the refueling stations of St1 Energy Company. Anhydrous E100 was delivered by North European Oil Trade (NEOT) Company in Finland. Deionized water was added into E100 to adjust water content to 4.4 % (m/m).

Two FFV cars were rented for the research project: Volkswagen Passat MultiFuel (DISI) and Ford Mondeo (MPFI), which are presented in Table 3.6.

3.2.2 Test matrix

Cars were tested on a chassis dynamometer in a climatic test cell at +23°C and -7°C. The cold-start tests were carried out by using the European exhaust emissions driving cycle, “NEDC”, which is defined in the UN ECE R83 regulation (Figure 3.1). NEDC totals 11.0 km, divided into three test phases to study emissions at cold start and with warmed-up engines. The first and second test phases each consisted of 2.026 km driving, and the third test phase, the extra-urban driving cycle (EUDC), was 6.955 km.

Table 3.6 Test cars at VTT

	FFV-DISI	**FFV-MPI**
Model year	2011	2010
Technology	1.4 litre turbo-charged DISI engine, 7 gear dual clutch autom. Transmission	2.0 litre natural aspirated MPI engine, 5 gear manual transmission
Weight	1557 kg	1477 kg
Odometer reading	48 700 km	43 600 km
Emission level	Euro 5	Euro 4

In addition to “NEDC” test, also the hot-start test was applied to monitor how warmed-up cars performed. For this purpose, the FTP75 city driving cycle was run as a hot-start test, even though it is a cold-start test according to the definition by the US Environmental Protection Agency (EPA). FTP75 driving cycle totals 17.77 km, which is divided into three test phases including a 600 seconds pause (Figure 3.1).

Measurements were carried out over four weeks in September – October 2013. Daily sequence of tests with both cars was as follows:

- Cold-start European test “NEDC”
- “Dummy” test (FTP75) to stabilize cars for the actual hot-start test
- Hot-start FTP75 test

The first FTP75 test was run as a “dummy” to assure that cars were sufficiently warm, and to improve repeatability of tests. C1-C8 hydrocarbons and aldehydes were analyzed only over the European NEDC driving cycle.

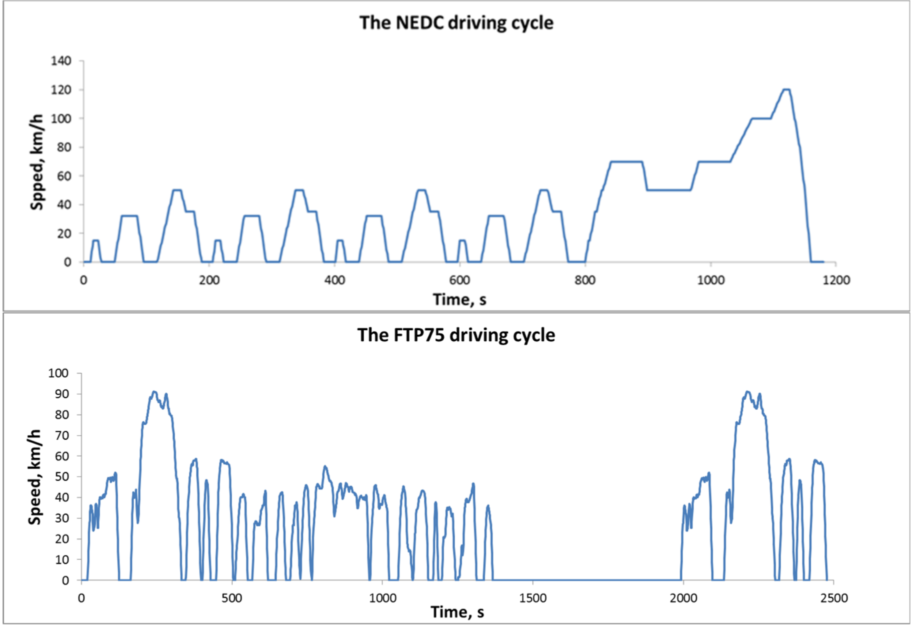


Figure 3.1 The NEDC and FTP75 driving cycles

Test matrix is shown in Table 3.7. Finnish contribution covered emission investigation with two cars, three fuels (E10, E85, and E100), two temperatures (+23°C and -7°C) and two test cycles (NEDC, FTP). The E100 fuel was tested only at temperature of +23°C, because the startability limit of neat ethanol is only around +12°C.

Table 3.7 Test matrix at VTT *) **)

	European test cycle			FTP hot-start test	
	E10	E85	E100*	E10	E85
	+23 and -7 °C	+23 and -7 °C	+23 °C	+23 and -7 °C	+23 and -7 °C
CO, HC, NO_x, CO_2, PM	2+2	2+2	2	2+2	2+2
C1-C8 hydrocarbons	2+2	2+2	2	-	-
Aldehydes	2+2	2+2	2	-	-
Multicomponent FTIR	2+2	2+2	2	2+2	2+2

*) The startability limit of neat ethanol is around +12 °C. Therefore E100 is not tested at -7 °C.

**) Additional steady-state tests were carried out for the particle characterization.

3.2.3 Analysis Methods

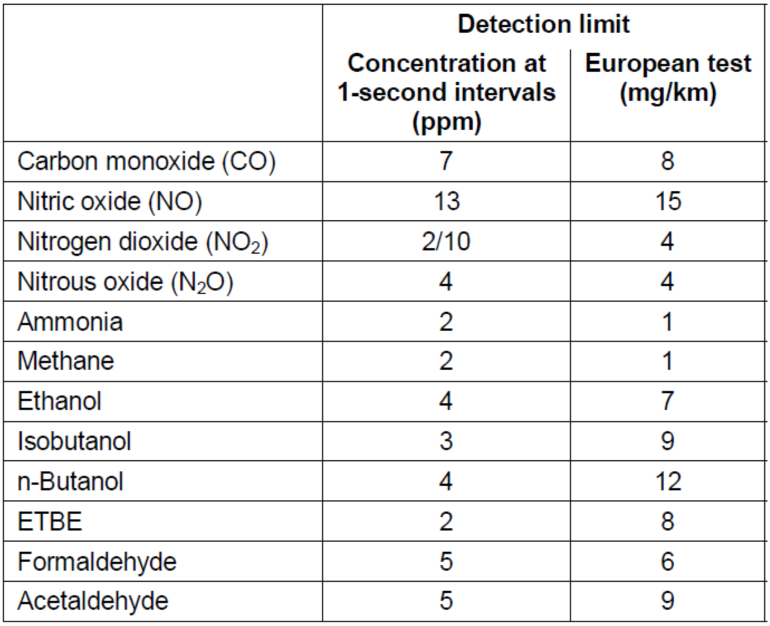
Gaseous regulated emissions. Equipment used in the measurement of the CO, HC, and NO_X emissions conforms to the specifications of the Directive 70/220/EEC and its amendments. The basic equipment are dynamometer Froude Consine 1.0 m, DC, 100 kW, constant volume sampler (CVS) AVL CVS i60 LD, Venturi-type and Pierburg AMA 2000, triple bench for gaseous regulated emissions. The true oxygen contents and densities of the fuels were used in the calculation of the results. A flame ionization detector (FID) used for measurement of hydrocarbons detects all carbon-containing compounds, also oxygenates (Sandström-Dahl et al. 2010). The calculation method chosen uses the density of 0.619 g/dm^3 (different from the EC regulation 692/2008).

C1 to C8 hydrocarbons. The diluted exhaust gas for analysis of C1 to C8 hydrocarbons are collected from the same Tedlar bags that are used for measurement of the regulated emissions, and fed to the gas chromatograph, (HP 5890 Series II, AL_2O_3, KCl/PLOT column, an external standard method). The hydrocarbons analysed are methane, ethane, ethene, propane, propene, acetylene, isobutene, 1,3-butadiene, benzene, toluene, ethyl benzene and m-, p- and o-xylenes. The detection limit is 0.02 mol-ppm, which corresponds to approximately 0.1 mg/km for methane, 0.5 mg/km for 1,3-butadiene and 0.7 mg/km for benzene.

Aldehydes are collected from the CVS diluted exhaust gas using 2,4-dinitrophenylhydrazine (DNPH) cartridges. The DNPH derivatives are extracted with an acetonitrile/water mixture and analysed using HPLC technology (Agilent 1260, UV detector, Nova-Pak C18 column). Aldehydes analysed are formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, methacrolein, butyraldehyde, benzaldehyde, valeraldehyde, m-tolualdehyde and hexanal. The detection limit for aldehydes corresponds to approximately 0.01 mg/km.

Multi-component analysis. A number of compounds were measured on-line using Fourier transformation infrared (FTIR) equipment (Gasmet Cr-2000). More than 10 exhaust components from the raw exhaust gas were measured at two-second intervals. The concentrations of many compounds are low with gasoline-fuelled cars when compared to detection limits (Table 3.8). These detection limits were converted to corresponding mass-based emissions representing the duration of the European test cycle with certain assumptions.

Table 3.8 Detection limits determined from manufacturer's reference spectra at one-second intervals as concentrations and calculated mass emissions over the European test cycle (Aakko-Saksa et al. 2011).



	Detection limit	
	Concentration at 1-second intervals (ppm)	**European test (mg/km)**
Carbon monoxide (CO)	7	8
Nitric oxide (NO)	13	15
Nitrogen dioxide (NO_2)	2/10	4
Nitrous oxide (N_2O)	4	4
Ammonia	2	1
Methane	2	1
Ethanol	4	7
Isobutanol	3	9
n-Butanol	4	12
ETBE	2	8
Formaldehyde	5	6
Acetaldehyde	5	9

Particulate matter. Particles were collected with an in-house designed high-capacity sampler (Kokko et al. 2000), which includes a dilution tunnel (Ø265 mm), a sample probe (Ø80 mm), two filter holders in parallel (Ø142 mm), a blower (Siemens ELMO-G, 2BH1 810-1HC36, 11 kW), a flow meter (Bronkhorst F-106C1-HD-V-12) and a controller (Stafsjö MV-E-80-P-TY-AC100-PN10). The sample flow can be controlled up to 2000 liters/minute to obtain appropriate particulate masses. In these measurements, a flow is 850–1200 litres/minute and two Ø142 mm filters are used in parallel. The filter type was Fluoropore 3.0 µm FSLW. A Sartorius SE2-F microbalance was used for weighing.

Real-time *particle number size distributions* by using Electrical Low

Pressure Impactor (ELPI, >8 nm) equipment by VTT after the TUT's dilution system shown in Figure 3 to validate stability of the measurements and to screen tailpipe particle emissions. In Europe, a particle number limit applies to the Euro 5/6 emission level light-duty vehicles with certain exceptions. The procedure takes into account only solid "dry" particles as the volatile portion of particles is evaporated before the measurement. The particle number measurements with ELPI at VTT took into account total number of "wet" particles. Therefore the European PN limit of 5×10^{11} #/km is not relevant for the results of this report.

In-depth analyses of nanoparticle formation and of secondary organic aerosols were carried out by the Tampere University of Technology (TUT) and the Finnish Meteorological Institute (FMI). Primary (tailpipe) emissions go through atmospheric transformations leading to secondary emissions. FMI and TUT studied this phenomena by using the Potential Aerosol Mass (PAM) chamber to oxidize primary emissions into secondary organic aerosols (SOA). Measurements were carried out before and after the PAM chamber.

FMI characterized before and after PAM from sub-micron PM: organics, sulfate, nitrate, ammonium, chloride, black carbon and metals (e.g. Ni, V, Ba, Cr, Fe, etc) with time resolution of 5 seconds by using the SP-AMS equipment (Figure 3.2).

TUT focused on in-depth characterization of particles by on-line detection of particle number sizes and number concentrations as "particle maps". In addition to primary particles, also secondary aerosol formed in atmospheric reactions is studied (after PAM chamber). TUT's test set-up for exhaust dilution and measurements is shown in Figure 3.3. An example of "particle maps", which will be analysed in the scientific articles, is presented in Figure 3.4. Some reports are already available [71-74].

Figure 3.2 FMI characterized before and after PAM from sub-micron PM: organics, sulfate, nitrate, ammonium, chloride, black carbon and metals.

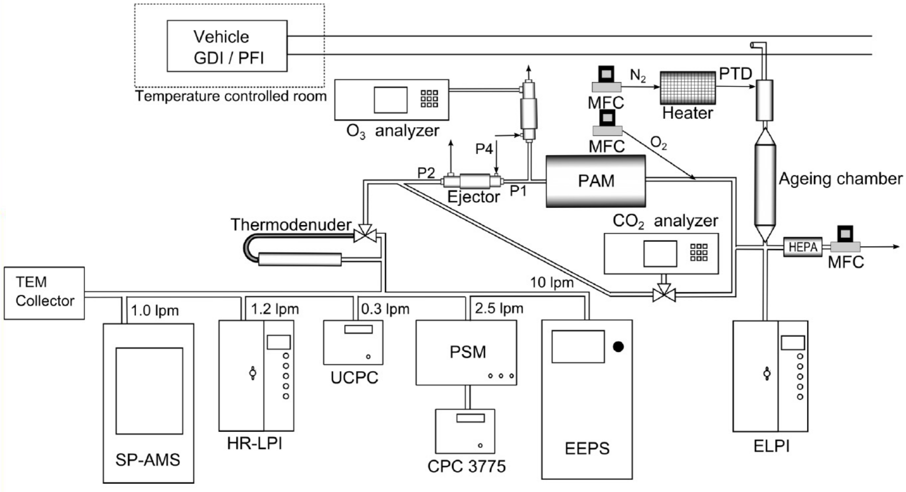


Figure 3.3 TUT test set-up for in-depth characterization of particles.

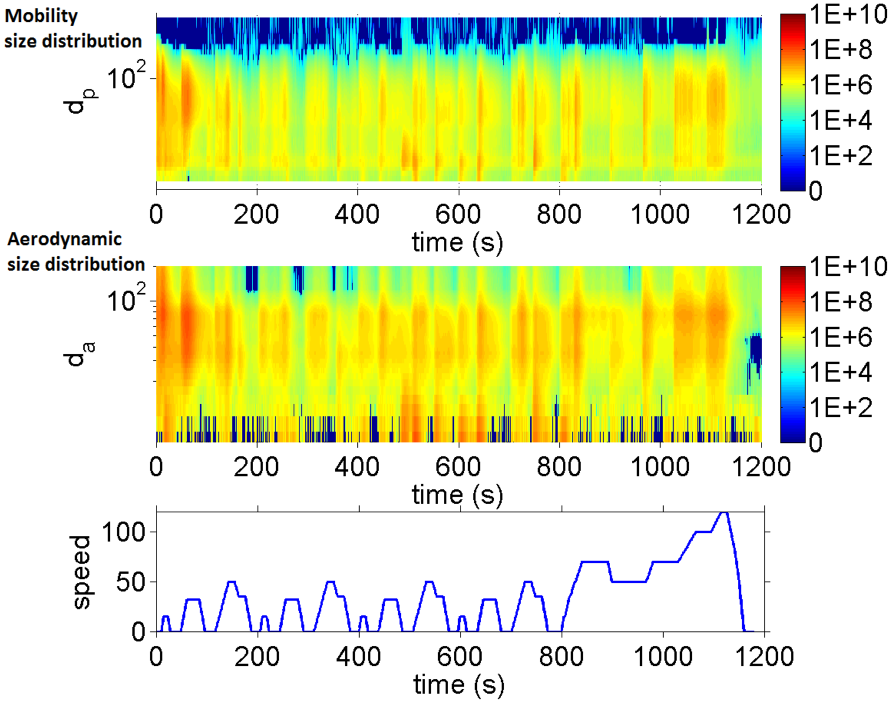


Figure 3.4 An example of “particle maps” from TUT measurements.

3.3 China

In accordance with 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.

3.3.1 Test vehicles

The tested vehicles are two 2011 year 1.6L AT light-duty vehicles of the same model with PFI engines and two 2010 year 1.4T AT light-duty vehicles of the same model with GDI engines. The mileage of 1# tested vehicle is approximately 11,000 kilometres and 2# tested vehicle is 22,000km. The mileage of 3# tested vehicle is approximately 24,000 kilometres and 4# tested vehicle is 41,000km.1# tested vehicle used pure gasoline, M15, and M30 fuels. 2 # tested vehicle used pure gasoline, E10, and E20 fuels. 3# tested vehicle used pure gasoline, M15, and M30 fuels. 4 # tested vehicle used pure gasoline, E10, and E20 fuels. The parameters of tested vehicles are shown in Table 3.9.

Table 3.9 Test Vehicles Parameters

Vehicle ID	1#, 2#	3#, 4#
Curb Weight (kg)	1285	1470
Displacement (L)	1.6	1.4
Engine Type	Naturally aspirated	Turbo charging
Maximum Power (kW)	77	96
Maximum Torque (N·m)	155	198
Fuel Label	93#	93#
Emission Standard	Euro Ⅳ + OBD	Euro Ⅳ + OBD

3.3.2 Test 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 3.10.

Table 3.10 Test Fuels Parameters

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

3.3.3 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 3.11.

Table 3.11 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

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.

3.3.4 Analysis methods of Instantaneous Emissions

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 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 CO_2 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), CO_2(MEXA), and HC(MEXA).

In FTIR method instantaneous values of CO, NO_X, CO_2, and CH_4 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 CO_2, 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), CO_2(FTIR), and CH_4(FTIR).

The instantaneous emissions of CH_3OH, HCHO, CH_3CHO, C_6H_6, C_7H_8, C_2H_4, C_3H_6, 1,3-C_4H_6, and iso-C_4H_8 unregulated pollutants before the dilution are measured by MEXA-6000FT (FTIR method).

3.3.5 Analysis methods of 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 CH_4 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, CO_2, and CH_4 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, CO_2, 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.

3.3.6 Analysis methods of 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, CO_2, and CH_4 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).

3.4 Israel

The study of Israel was focused on comparative research on the emissions from vehicles equipped with SI engines that comply with different emission standards (Euro 6, Euro 5, and Euro 3) and feature different combustion technologies (direct injection and port fuel injection), using various fuels (RON 95, M15, and E10). The tests were performed using a conventional state-of-the-art emissions test facility equipped with a chassis dynamometer and the measuring equipment needed for emissions testing according to the European emissions legislation. Two different driving cycles were used: NEDC and US06. During the campaign, four vehicles were tested.

3.4.1 Experimental set-up

The measurements were carried out in the Vehicle Emissions Laboratory (VELA) of the Joint Research Centre in Ispra (Italy). The emissions test facility used for the experimental campaign is in full compliance with the emissions requirements set by the legislative procedure for vehicle type approval. The facility consists of a climatic chamber, a roller bench, and the equipment for emissions measurement. All tests were carried out at a temperature of 22°C ± 1°C. In order to follow driving cycles as defined in the legislation, the driver was assisted by a driver aid system. Regulated pollutant emissions were measured according to the legislative Type I test procedure (UNECE Regulation 83) using a constant volume system (CVS) based on a full flow dilution tunnel with a critical flow Venturi.

Emissions were measured using the following analyzers/methodologies:

- Carbonyls were sampled using SiO2–C18 cartridges (Waters Sep-Pak Classic) coated with 2,4 dinitrophenylhydrazine (DNPH) under stable temperature and humidity conditions after passing through the dilution tunnel and analyzed by high-performance liquid chromatography (HPLC-Agilent 110 Series) with UV detection. The carbonyls were trapped by reaction with DNPH inside the cartridges to form the corresponding 2,4-dinitrophenylhydrazone derivatives. A commercial hydrazone standard mixing solution (SUPELCO CARBCarbonyl DNPH Mix 1) was used. The standard contained the addressed aldehydes in the corresponding DNPH hydrazone derivative compound (formaldehyde and acetaldehyde) as well as other derivatives of interest in this group, namely: acetone, acrolein, propionaldehyde, butyraldehyde, and benzaldehyde. Seven-point calibration curves were constructed between 0 and 2 mg L−1, using a correlation coefficient better than 0.99 as acceptable criteria.

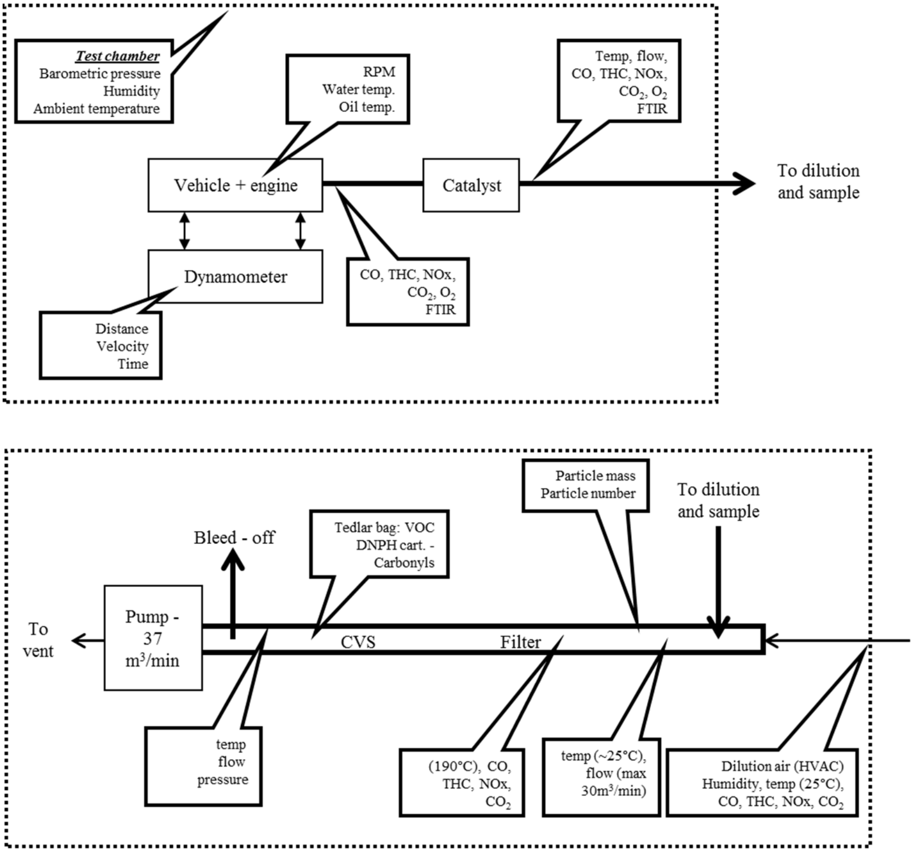


Figure 3.5 Schematic of the VELA Emissions Test Facility.

According to the test protocol, the test vehicles were required to be in good mechanical condition and preferably to have completed at least 1,000 km on the fuel recommended by the manufacturer prior to testing in order to ensure that the catalyst was adequately aged and the engine combustion chamber deposits had stabilized. For all of the vehicles, the engine oil, oil filter, and air filter were changed before starting the test program. After the oil change, the oil was aged by the vehicle being driven a minimum of 500 km on the dynamometer. The fuel used for oil aging was Fuel 1 from the test fuel matrix (RON95). The engine oil complied with the grade recommended by the vehicle manufacturer.

In addition, the following operations were performed on each vehicle:

- The exhaust system of the vehicle was checked for leaks.
- The engine was checked for leaks of the gasoline/lubricant circuit.
- When necessary, additional fittings, adapters, or devices were fitted to the fuel system in order to allow complete drainage of the fuel tank, which was, in general, accomplished by means of the vehicle fuel pump.
- When possible, the engine was equipped with suitable thermocouples to monitor the lubricant and coolant temperature.

3.4.2 Tested fuels

Three fuels were tested:

- RON95 – regular gasoline.
- M15 – 85% gasoline and 15% methanol.
- E10 – 90% gasoline and 10% ethanol.

The properties of the different fuels are detailed at table 3.12.

Table 3.12 Properties of the tested fuels

		Ron 95	**M15**	**E10**
Research octane number		96.6	96.7	95.4
Motor octane number		86.5	85	85.7
Benzene	%V/V	0.37	0.34	
Total aromatics	%V/V	29.3	25.1	25.6

Total olefins	%V/V	11.3	10.3	7.5
Total oxygenates	%V/V	8.3	14.9	
Total saturated	%V/V	51.1	49.7	
Total oxygen	%m/m	1.61	7.77	3.3
MTBE	%V/V	8.14	0.27	
ETBE	%V/V	0.2		
Methanol	%V/V		14.38	
Ethanol	%V/V			9.28
Iso-Butanol	%V/V		0.06	
Other oxygenates	%V/V		0.17	
Carbon	%m/m	84.84	78.9	83.3
Hydrogen	%m/m	13.55	13.3	13.3
Oxygen	%m/m	1.61	7.8	3.4
HHV	kcal/kg	10877	10084	
LHV	kcal/kg	10190	9412	10015
Density	kg/CM (@15°C)	738.3	741.8	745

3.4.3 Test cycles

Emissions of the test vehicles were measured over two different driving cycles:

- The New European Driving Cycle (NEDC), which is the legislative cycle for type approval of European passenger cars. This is a cold start cycle and all the tests performed using it were carried out after the vehicle had experienced an overnight soaking period. The NEDC consists of two parts: four repeated urban driving cycles (UDC, also ECE-15) and an extra-urban driving cycle (EUDC).
- The US06 part of the US Supplemental FTP (SFTP) Driving Schedule is representative of aggressive, high speed and/or high acceleration driving behavior. The US06 cycle is a hot start cycle that requires the vehicle be run after a pre-conditioning cycle before starting the emissions

measurement. According to the US legislation, different cycles, including the US06 driving cycle, can be used for vehicle pre-conditioning, and this option was selected for these tests.

3.4.4 Test vehicles

Table 3.13 Test Vehicles

	Vehicle 1	**Vehicle 2**	**Vehicle 3**	**Vehicle 4**
Emission level	Euro 5	Euro 5	Euro 3	Euro 6
Injection type	Port fuel injection	Direct injection	Port fuel injection	Port fuel injection
Combustion	Stoichiometric	Stoichiometric	Stoichiometric	Stoichiometric
Air intake	Naturally aspirated	Turbocharged	Naturally aspirated	Naturally aspirated
Gearshift	Automatic transmission	Robotic transmission	Manual transmission	Manual transmission
Inertia class (kg)	1250	1360	1250	1020
Engine displacement	1.6 liter	1.8 liter	1.6 liter	1.2 liter
Mileage	27222	58005	139592	1145

3.4.5 Test protocol

To ensure that sufficient and reliable data were obtained to determine fuel effects, it was decided to design the test protocol on the basis of the following criteria:

- True (long-term) repeat tests must be conducted.
- The order of the test fuels must be randomized to avoid bias

due to engine drift.

- Sufficient and appropriate vehicle conditioning must be performed to compensate for the continual changes in test fuels.

It was decided to carry out at least three long-term repeats. The test order had to be randomized to prevent bias due to vehicle drift or other time-related effects. The resulting test order is shown in the table below (Table 3.14).

Table 3.14 Test Order

Day 5	Day 4	Day 3	Day 2	Day 1	
1	2	3	2	1	Week 1
1	3	2	1	3	Week 2
			3	2	Week 3

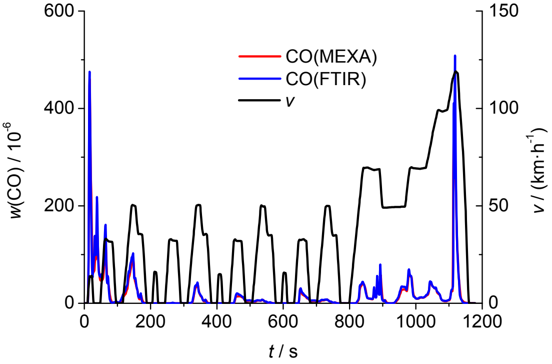
Chapter 4 Comparison Results of Different Analysis Methods

In order to verify the accuracy and consistency of the various measurement methods, instantaneous emissions of CO, CO_2, and NO_X pollutants as well as cycle average emissions of CO, CO_2, NO_X, formaldehyde, acetaldehyde, benzene, and toluene pollutants are compared in Chapter 4.

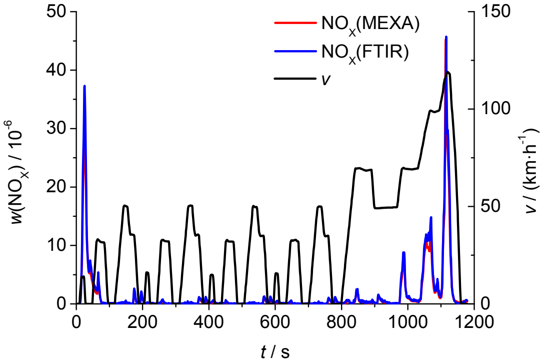
4.1 Instantaneous Regulated Emissions

Comparatively analysis of the measurement results of M30 and E20 fuels, the instantaneous emissions curves of CO, NO_X, and CO_2 during the entire NEDC are measured by MEXA and FTIR two kinds of methods, as shown in Figure 4.1(a)~(c) and Figure 4.2(a)~(c).

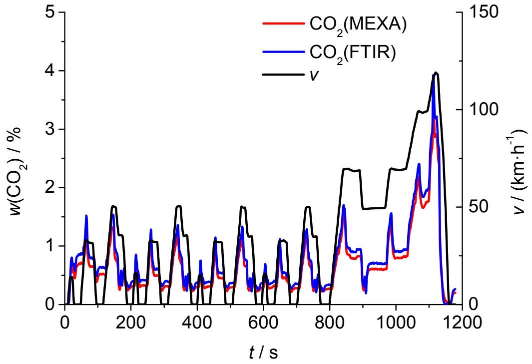
As shown in Figure 4.1(a)~(b) and Figure 4.2(a)~(b), for either M30 fuel or E20 fuel, the curve shape and numerical size of CO and NOX instantaneous emissions curves measured by two methods are basically the same. Even during the first 100s when the variation of emissions is largest and the last 200s 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.



(a) CO

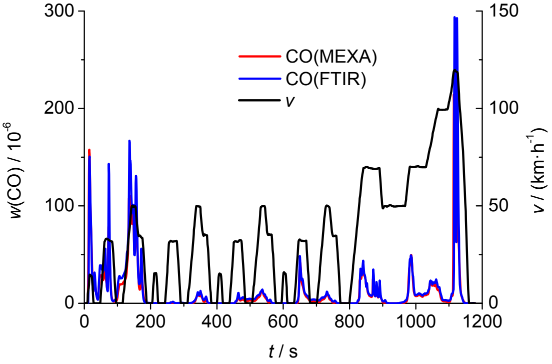


(b) NO_X

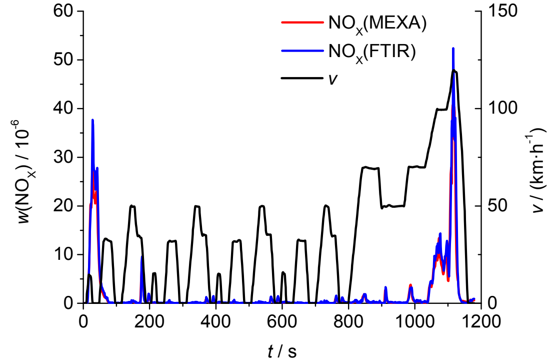


(c) CO_2

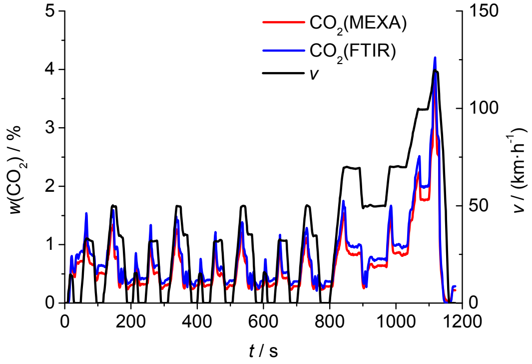
Figure 4.1. Instantaneous emissions curves of regulated pollutants of M30 fuel (MEXA and FTIR methods)



(a) CO



(b) NO_X



(c) CO_2

Figure 4.2. Instantaneous emissions curves of regulated pollutants of E20 fuel (MEXA and FTIR methods)

Shown in Figure 4.1(c) and Figure 4.2(c), CO_2(FTIR) is slightly bigger than CO_2(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 CO_2 which has the biggest emission values.

4.2 Cycle Average Regulated Emissions

Comparatively analysis of the measurement results of M30 and E20 fuels, the cycle average emissions of CO, NO_X, and CO_2 are measured by MEXA analysis of bag sampling, integral of FTIR instantaneous values, and integral of MEXA instantaneous values three kinds of methods, as shown in Figure 4.3 and Figure 4.4.

Seeing from Figure 4.3 and Figure 4.4, for M30 fuel or E20 fuel, the measuring results of CO, CO_2, and NO_X regulated emissions of the three methods are in the same order, which is integral results of FTIR instantaneous values > MEXA analysis results of bag sampling > integral results of MEXA instantaneous values. This is consistent with the instantaneous results shown in Figure 4.1 and Figure 4.2. Overall, as the MEXA analysis of bag sampling method is the specified method in the EU RC83-05 standard, it could indeed measure the average emissions of regulated pollutants.

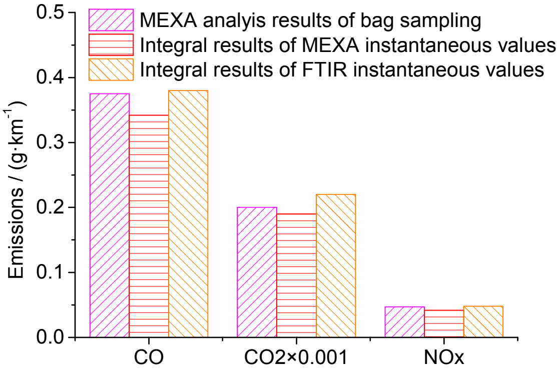


Figure 4.3. Comparatively analysis of cycle average regulated emissions of M30 fuel measured by three methods

In order to more accurately assess the consistency of the different test methods, the average value of the test results of three methods is defined as the standard value. The relative deviations of CO, CO_2, NO_X average emissions of gasoline, M15, and M30 fuels measured by various methods are calculated, as shown in Table 4.1. The relative deviation of those of gasoline, E10, and E20 fuels are also calculated, as shown in Table 4.2. For CO, CO_2, and NO_X regulated emissions of gasoline, M15, M30, E10, and E20 five fuels, the MEXA analysis results of bag sampling are all in the middle. The calculation results indicate that the deviation of three methods measuring results of average regulated emissions is basically within the range of ± 10%.

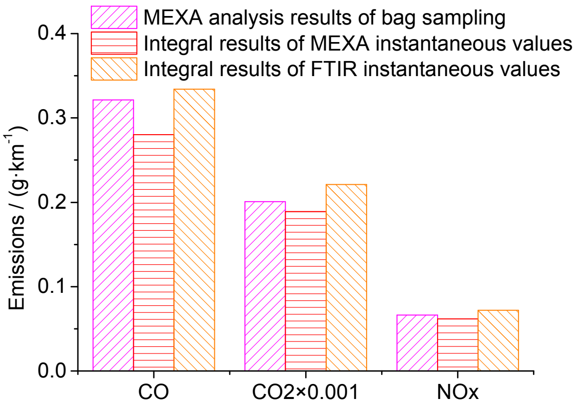


Figure 4.4. Comparatively analysis of cycle average regulated emissions of E20 fuel measured by three methods

Table 4.1. Deviations of cycle average regulated emissions of M30 fuel measured by three methods

Pollutants	Measurement Methods	Deviations (%)		
		Gasoline	M15	M30
CO	MEXA analysis of bag sampling	1.8	1.0	2.5
	Integral of MEXA instantaneous values	-6.4	-7.0	-6.4
	Integral of FTIR instantaneous values	4.6	5.9	3.9
CO_2	MEXA analysis of bag sampling	-2.2	-1.7	-1.6
	Integral of MEXA instantaneous values	-6.6	-6.8	-6.7
	Integral of FTIR instantaneous values	8.8	8.5	8.3
NO_X	MEXA analysis of bag sampling	-0.2	-0.9	2.8
	Integral of MEXA instantaneous values	-7.8	-4.4	-8.5
	Integral of FTIR instantaneous values	8.0	5.3	5.7

Table 4.2. Deviations of cycle average regulated emissions of E20 fuel measured by three methods

Pollutants	Measurement Methods	Deviations (%)		
		Gasoline	E10	E20
CO	MEXA analysis of bag sampling	3.5	5.0	3.0
	Integral of MEXA instantaneous values	-10.9	-11.0	-10.2
	Integral of FTIR instantaneous values	7.4	6.0	7.1
CO_2	MEXA analysis of bag sampling	-2.9	-2.6	-1.4
	Integral of MEXA instantaneous values	-7.2	-6.7	-7.2
	Integral of FTIR instantaneous values	10.1	9.3	8.6
NO_X	MEXA analysis of bag sampling	-0.6	1.1	-0.5
	Integral of MEXA instantaneous values	-8.8	-7.9	-7.4
	Integral of FTIR instantaneous values	9.3	6.8	7.9

4.3 Cycle Average Unregulated Emissions

Comparatively analysis of the measurement results of M30 and E20 fuels, the cycle average emissions of formaldehyde, acetaldehyde, benzene, and toluene pollutants during the NEDC are measured by two kinds of methods, as shown in Figure 4.5 and Figure 4.6. Seeing from the figures, for formaldehyde, acetaldehyde, benzene, and toluene emissions, the integral results of FTIR instantaneous values, chemical analysis results of bag sampling 1, and chemical analysis results of bag sampling 2 are basically the same.

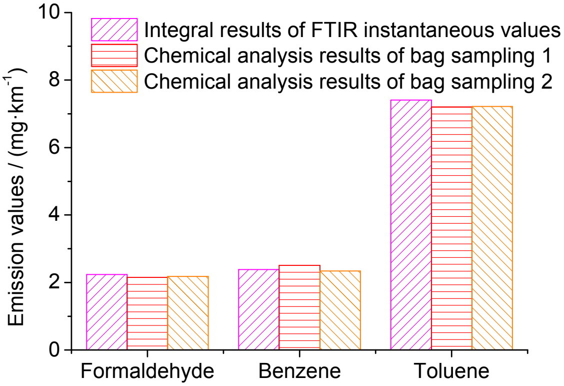


Figure 4.5. Comparatively analysis of cycle average unregulated emissions of M30 measured by various methods

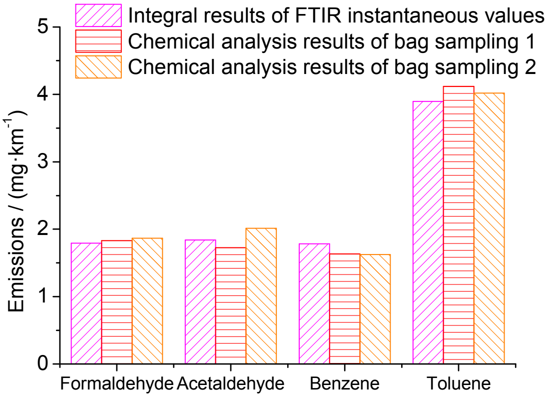


Figure 4.6. Comparatively analysis of cycle average unregulated emissions of E20 measured by various methods

The average value of the integral results of FTIR instantaneous values, the chemical analysis results of bag sampling 1, and the chemical analysis results of bag sampling 2 is defined as the standard value. The relative deviations of cycle average unregulated emissions of gasoline, M15, and M30 fuels measured by various methods are calculated, as shown in Table 4.3. The relative deviation of those of gasoline, E10, and E20 fuels are also calculated, as shown in Table 4.4. The results indicate that the deviations of various methods measuring results of cycle average unregulated emissions are basically within the range of ± 10%.

Table 4.3. Deviations of cycle average unregulated emissions of M30 by various methods

Pollutants	Measurement Methods	Deviations (%)		
		Gasoline	M15	M30
Formaldehyde	Integral of FTIR instantaneous values	0.1	-1.1	2.4
	Chemical analysis of bag sampling 1	1.7	1.0	-1.9
	Chemical analysis of bag sampling 2	-1.8	0.1	-0.5
Benzene	Integral of FTIR instantaneous values	6.5	-1.5	-1.4
	Chemical analysis of bag sampling 1	0.8	-0.2	4.3
	Chemical analysis of bag sampling 2	-7.3	1.7	-2.9
Toluene	Integral of FTIR instantaneous values	2.4	1.5	1.8
	Chemical analysis of bag sampling 1	-1.8	-1.3	-1.1
	Chemical analysis of bag sampling 2	-0.7	-0.3	-0.8

Table 4.4. Deviations of cycle average unregulated emissions of E20 by various methods

Pollutants	Measurement Methods	Deviations (%)		
		Gasoline	E10	E20
Formaldehyde	Integral of FTIR instantaneous values	-0.3	-2.2	-1.9
	Chemical analysis of bag sampling 1	-4.9	-7.5	0.0
	Chemical analysis of bag sampling 2	5.2	9.6	1.9
Acetaldehyde	Integral of FTIR instantaneous values	2.7	5.1	-1.1
	Chemical analysis of bag sampling 1	-9.8	-5.7	-7.2
	Chemical analysis of bag sampling 2	7.1	0.6	8.3
Benzene	Integral of FTIR instantaneous values	-0.4	0.5	6.2
	Chemical analysis of bag sampling 1	1.6	2.1	-2.8
	Chemical analysis of bag sampling 2	-1.2	-2.6	-3.3
Toluene	Integral of FTIR instantaneous values	0.4	-3.5	-2.9
	Chemical analysis of bag sampling 1	-2.6	1.1	2.7
	Chemical analysis of bag sampling 2	2.2	2.4	0.2

Chapter 5 Exhaust Emissions Results of Different Alcohol Fuels, Vehicles and Temperatures

This chapter mainly introduces the emissions tests of alcohol fueled vehicles on the chassis dynamometer at normal and low temperatures and researches the influences of key factors on the vehicle emissions performance. It mainly contains the influences of alcohol content in the fuels on regulated and unregulated pollutants emissions from light-duty vehicles at normal and low temperatures, the influences of ambient temperature on vehicle pollutants emissions, and the influences of engine types on vehicle regulated emissions, unregulated emission and particulate emissions.

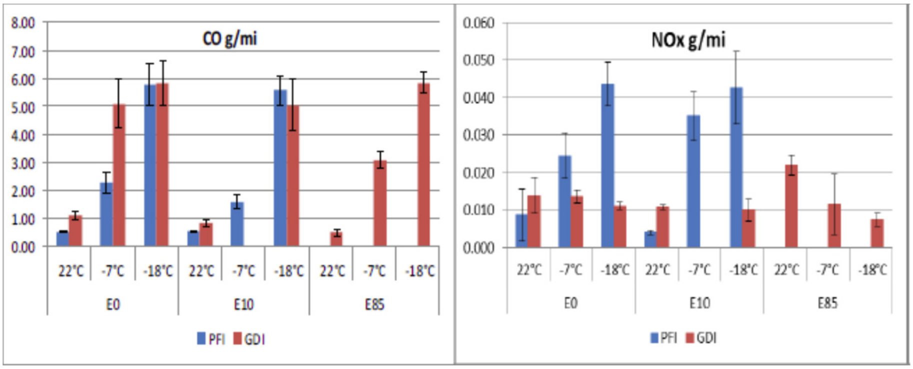
5.1 Canada

5.1.1 Test results of FTP-75 cycle

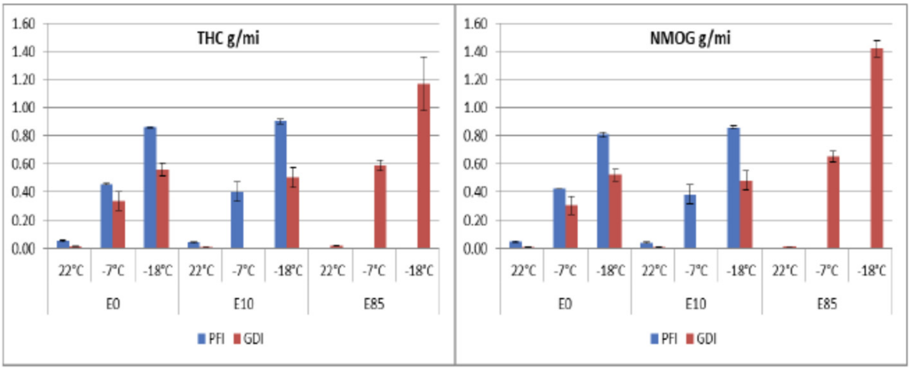
Figure 5.1~5.7 shows the test results of two vehicles (PFI and GDI) during the FTP-75 cycle, including regulated emissions, greenhouse gases, select carbonyl compounds, BTEX and other VOCs, organic carbon and elemental carbon, particle number emission rate and particle number size distribution.

Firstly, E10 fuel was compared to E0 (gasoline). In general there were very few significant changes in the gaseous emissions for either vehicle due to the use of E10. The largest differences measured due to the use of E10 were increases in the acetaldehyde and formaldehyde emissions rates of up to 594% and 124% respectively during cold temperature testing. The PFI acetaldehyde emission rate increased more than 100% at 22°C. The increases in carbonyls contributed to an increase in the NMOG and THC emission rates of 5% and 6%. A 4%

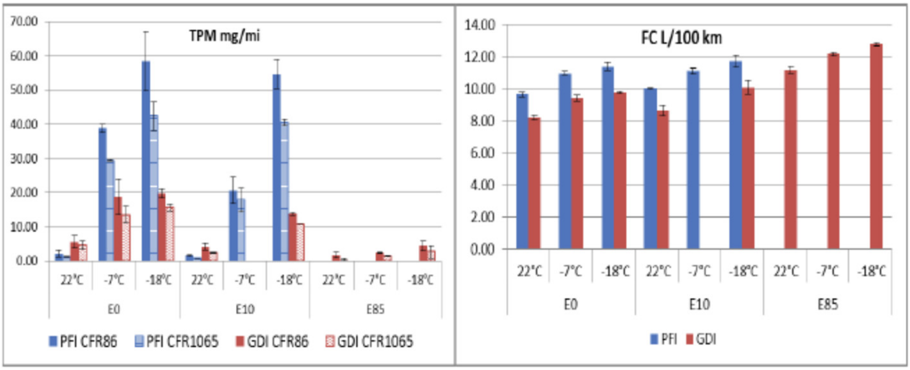
increase in fuel consumption was observed for the PFI at 22°C. There was a statistically significant decrease of 3% in the CO_2 emission rate for the PFI at -7°C. This equated to the same decrease in CO_2e as CO_2 is the most abundant of the three GHGs measured. The only statistically significant changes observed in the BTEX emission rates due to the use of the E10 fuel occurred for the GDI at 22°C where reductions of 38% to 65% were quantified. There also appeared to be reductions in the PFI BTEX emission rates over the same test condition but a statistical analysis was not conducted due to a sample size of only 1. There were significant reductions in the TPM emission rates for both vehicles due to the use of E10 over various test conditions. The PFI vehicle had lower TPM of 38% to 40% at 22°C and -7°C respectively. However there was no measurable difference at -18°C. The GDI TPM emission rate was reduced by 30% to 48% at 22°C and -18°C respectively. TPM was collected using two sampling methods and thus the delta TPM emission rates varied between the two methods. In general decreases in EC follow the same trends as the TPM. There were also reductions in the percent OC of the TC at -18°C for both vehicles. Although the above changes were observed in the TPM emission rates, the only significant change in the particle number emission rate was for the GDI at -18°C where a reduction of 27% was measured due to the use of the E10 fuel. There appeared to be a slight shift downwards in the primary peak diameter from 69nm to around 60nm for the PFI vehicle at 22°C when operated on E10 vs. E0.



(a) CO (b) NO$_X$



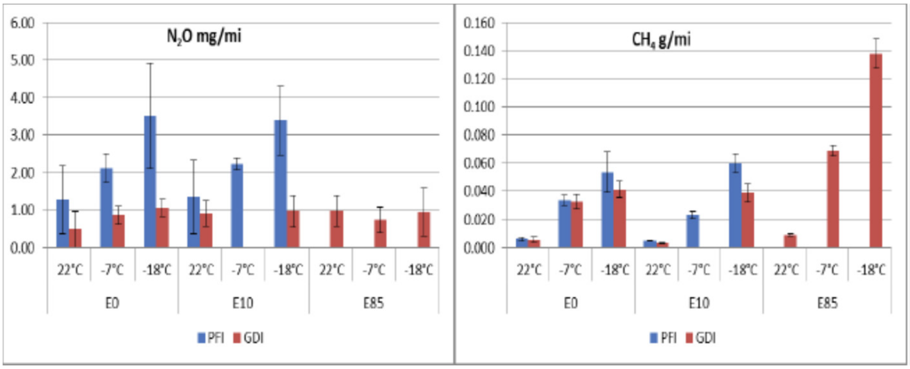
(c) THC (d) NMOG



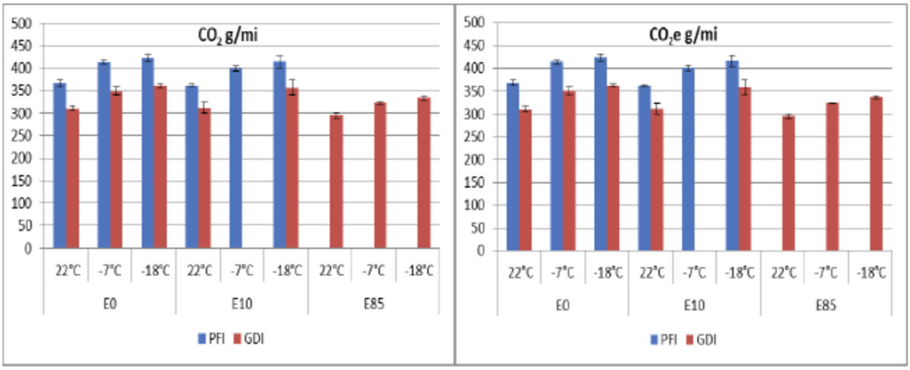
(e) TPM (f) Fuel Consumption

Figure 5.1. Regulated emissions and fuel consumption results of FTP-75 cycle

Secondly, the emissions results of E85 were compared to E0 fuel (GDI only). There were significant reductions in the CO emission rates of 56% and 40% at 22°C and -7°C respectively. However there was no measureable difference at -18°C. E85 appeared to increase the NO_X emission rate at 22°C but decrease it at -18°C. Statistically significant increases in THC and NMOG due to the use of the E85 fuel mainly during the cold start, were measured across all three test temperatures. These increases were due in part to the increase in carbonyl compounds as well as in the measured unburned ethanol which comprised 22% to almost 70%, from 22°C, to -18°C respectively, of the calculated NMOG emission rates. As expected, since the energy density of E85 fuels is lower than that of E0, there was a fuel consumption penalty of approximately 29% to 36%. The fuel penalty was higher for the 22°C tests as the E85sum fuel contained more ethanol by volume and had a lower net heating value. The use of E85 fuel as opposed to E0 led to reductions of 5% to 8% in CO_2 at 22°C and both cold temperatures. This CO_2 reduction translated into similar reductions in the CO_2e emission rate (5-7%) even though there were increases of 67%, 110%, and 235% in CH_4 at 22°C, -7°C and -18°C respectively. The emission rates of formaldehyde and acetaldehyde were 3 and 9 times higher respectively when the GDI vehicle was fuelled with E85 compared to E0 and tested at 22°C. The increases in emissions of these compounds were more pronounced at cold temperature, for example acetaldehyde was almost two orders of magnitude higher on E85 than on E0 at -18°C. BTEX emission rates were approximately 73% to 84% lower with use of the E85 fuel compared to E0 at 22°C. Reductions in BTEX by approximately 50% were also observed at -7°C and, to a lesser extent at-18°C, due to the use of the E85 fuel; however these reductions were not statistically significant at -18°C due to sample variability. Statistically significant reductions in TPM of 70% to 90% were observed over the three test temperatures due to the use of E85. Corresponding reductions of approximately 90% were observed in the EC and TC results indicating that the decrease in TPM was mainly due to a decrease in elemental carbon for some of the same reasons as mentioned below. The use of E85 with the GDI engine also decreased the particle number emission rate by 78% to 90% to the range of the particle number emission rate from the PFI vehicle on E0. These reductions were fairly uniform over all three phases of the FTP-75. There was also a shift to a lower primary peak diameter, from 70-80nm to as low as 34nm at 22°C, due to the use of E85. This reduction in particle number emissions with the use of mid to higher level ethanol blends has been reported elsewhere (Mamakos and Manfredi 2012, Yanowitz and McCormick 2009) and is thought to be owing in part to the lower sooting tendency of ethanol due to increased oxidation from higher levels of oxygen and to a reduced quantity of aromatics present in the blended fuel.



(a) N_2O (b) CH_4

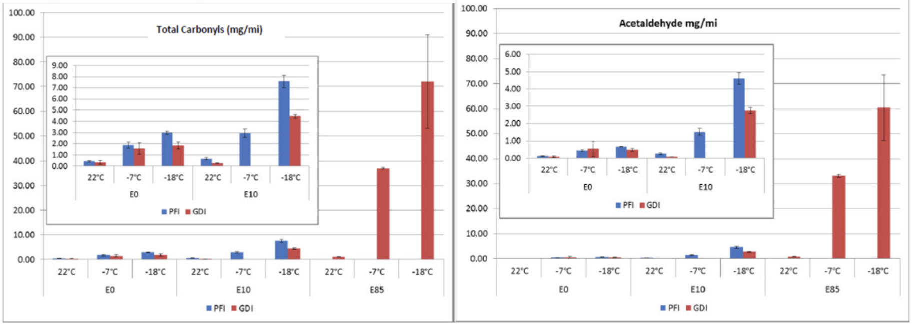


(c) CO_2 (d) CO_2e

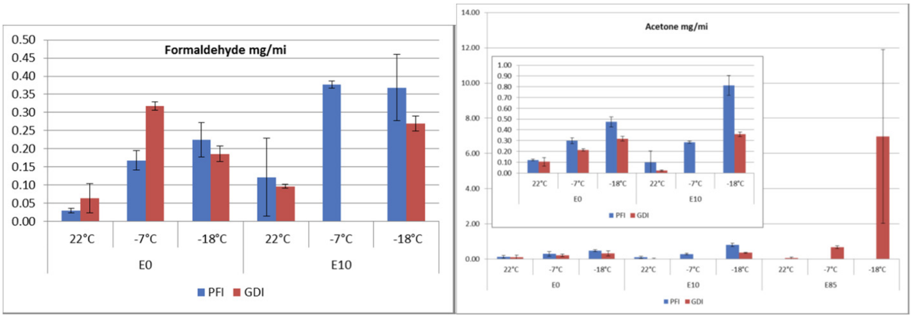
Figure 5.2. Greenhouse gases results of FTP-75 cycle

Emission results of the two vehicles (PFI and GDI) were also compared. The CO emission rates of the GDI at 22°C and -7°C were 105% and 124% higher than those of the PFI but still fell well below the standard. For the most part the remaining gaseous measurements including NMOG, carbonyl compounds, and BTEX were either unchanged or lower for the GDI by 29% to 150% depending on the test configuration. The GDI vehicle consumed approximately 15% less fuel over the FTP-75 regardless of the test cell temperature or test fuel (E0, E10). Similar decreases were observed in the CO_2 emission rates. There were statistically significant differences in the

CH_4 and N_2O emissions rates when both vehicles were operated on E10 at -18°C: the GDI emitted 36% to 72% less respectively. The GDI had 15% lower CO_2e emission rates over the test matrix except at the E10 22°C test condition; these reductions were largely influenced by similar reductions in CO_2. The GDI vehicle had approximately 200% higher averaged cycle TPM emission rates at 22°C than the PFI, however at both -7°C and -18°C the trend was reversed and the PFI vehicle emitted more than 2-3 times the amount of TPM. A similar pattern was seen with the TC emission rate where both OC and EC were observed to be lower at cold temperature when comparing the GDI to the PFI. It was also noted that the ratio of OC: EC increased from 10:90% to 41:59%: for the PFI while operated on E0 at -18°C. Although the TPM emission rate was lower for the GDI vehicle at both cold temperature conditions, the particle number emission rate was higher for the GDI vehicle across all three temperatures, by 615% to 32%, at 22°C and -18°C respectively, when the vehicles were fuelled with E0. It should be noted that the particle number emission rate is measured after the dilute exhaust passes through a thermodenuder which serves to remove volatile material and thus the make-up of the particles in the exhaust at the EEPS and at the TPM filter are not identical. Further discussion of the particle composition is presented in Chan et al. where it was found that while the solid particle number emissions of the GDI remained higher than the PFI, the amount of black carbon emitted by the GDI vehicle was significantly lower than from the PFI at cold temperature. Reasons given for this increase were possible differences in how the demands of the driving cycle may have been met by vehicles with different rated power, as well as differences in engine control strategies for cold start and driveablity. The peak diameters were similar for both vehicles at 22°C and were in the range of 70nm to 80nm; however there was a slight increase in the peak size for the PFI at cold temperature to just over 90nm.



(a) Total Carbonyls (b) Acetaldehyde



(c) Formaldehyde (d) Acetone

Figure 5.3. Select carbonyl compounds results of FTP-75 cycle

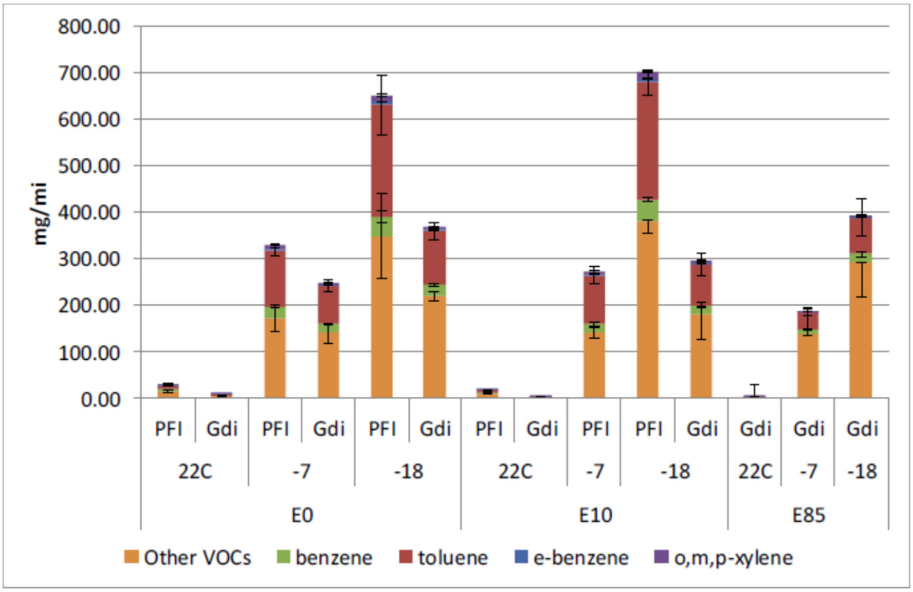


Figure 5.4. BTEX and other VOCs results of FTP-75 cycle

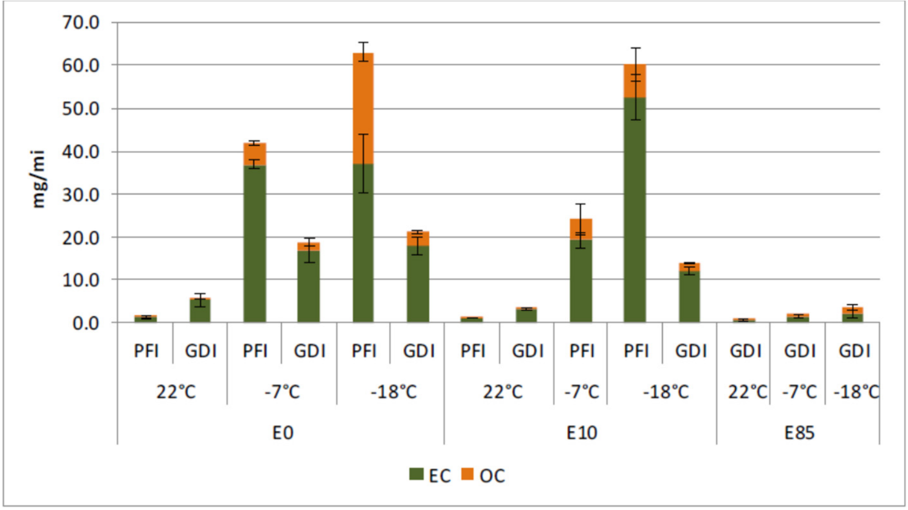


Figure 5.5. Organic carbon and elemental carbon results of FTP-75 cycle

The ambient temperature had a sufficient impact on all kinds of emissions from vehicles. As seen from Figure 5.1~5.7 there were significantly higher emission rates and fuel consumption at cold ambient temperature for both vehicles with the exception of N_2O, and in some cases NO_X. In general, it was found that the colder the temperature the higher the emission rate. As seen in previous PFI/GDI paired studies, the effect of the cold temperature testing was much smaller on the GDI TPM emission rate than on the PFI. For example, going from 22°C to -18°C the PFI TPM emission rate increased by almost 30 times whereas the GDI emission rate increased by only 3.5 times. In general a decrease in ambient temperature resulted in a shift to a slightly larger primary peak diameter; 60-70nm to 90nm for the PFI, and 70nm to 80nm for the GDI, when operated on both E0 and E10. At all test temperatures the use of E85 significantly reduced PM emissions. The cold temperature generally resulted in a shift to a slightly larger primary peak diameter, e.g. 35nm to approximately 50nm from 22°C to -18°C for E85, and 70nm to 80nm for E0.

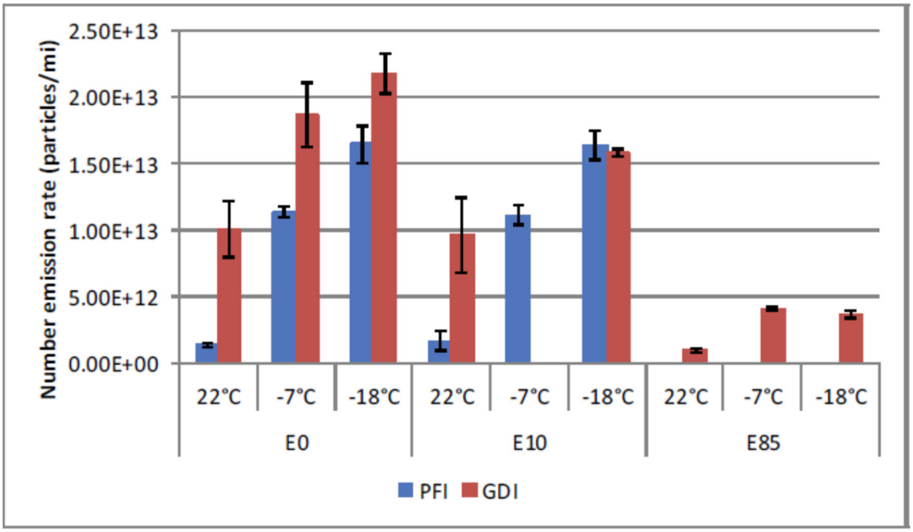
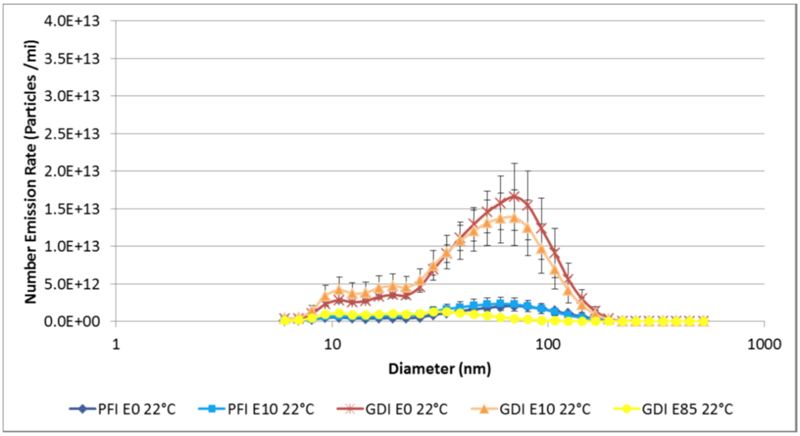
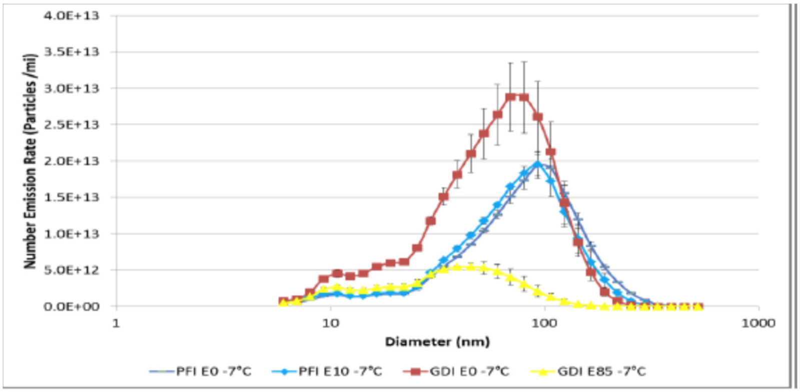


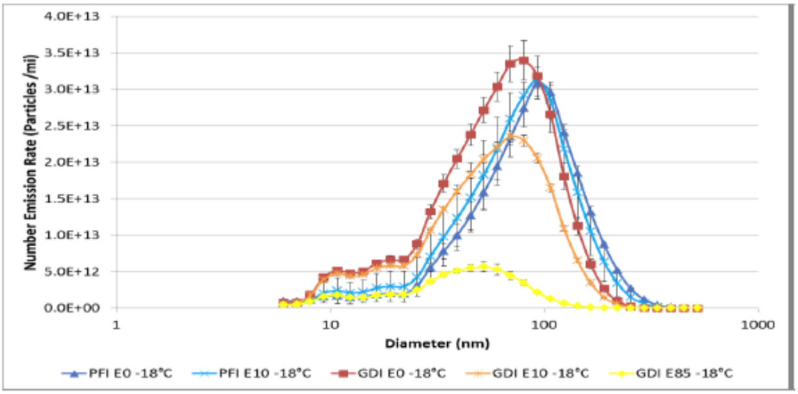
Figure 5.6. Particle number emission rate results of FTP-75 cycle



(a) 22°C



(b) -7°C



(c) -18°C

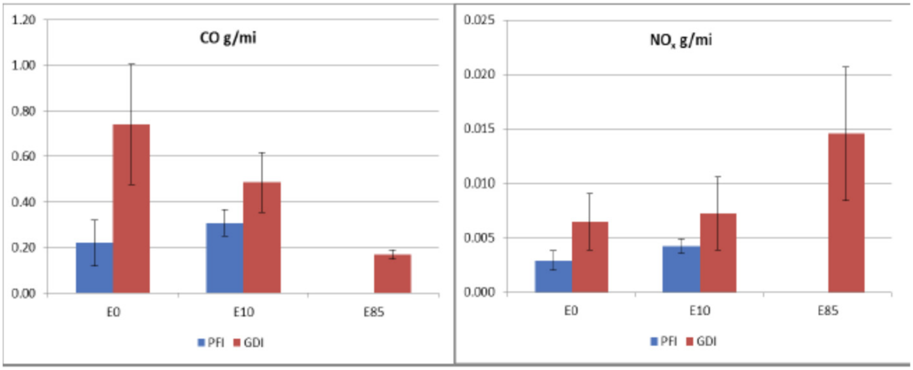
Figure 5.7. Particle number size distribution results of FTP-75 cycle

5.1.2 Test results of HWFCT cycle

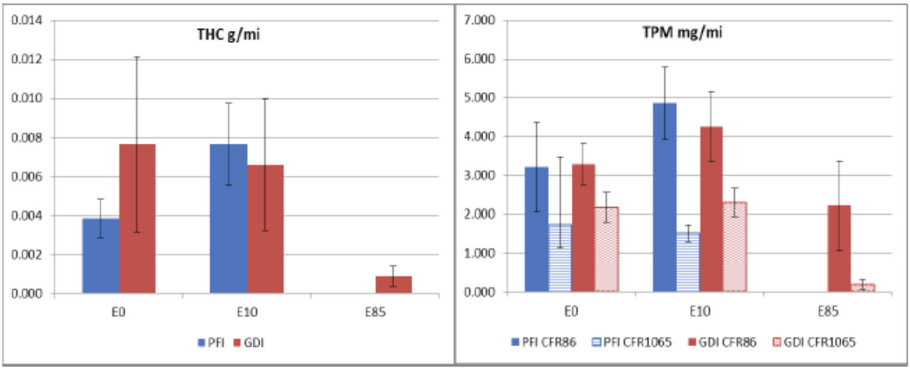
Figure 5.8 (a) ~ (f) shows the test results of two vehicles (PFI and GDI) during the HWFCT cycle at normal temperature, including regulated emissions and fuel consumption.

Firstly, the impact of ethanol content proportion in fuels on HWFCT emissions was analyzed. Figure 5.8 shows that generally there were no significant differences due to the use of the E10 fuel. There were however significant reductions ranging from 77% to 89% in CO, THC, and TPM (40CFR1065) due to the use of E85. As seen over the FTP-75 composite there was a 32% increase in fuel consumption, but an 8% decrease in CO_2.

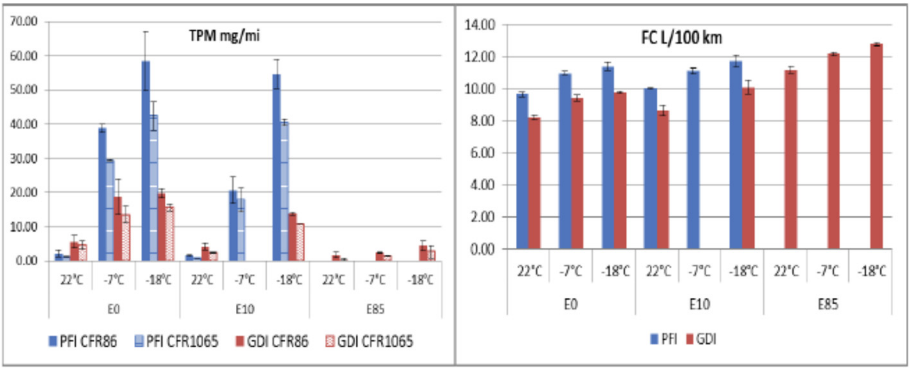
Secondly, the emissions results of PFI and GDI vehicles during the HWCFT cycle were compared. As seen in Figure 5.8, the GDI vehicle had higher CO and NO_X emissions than the PFI however the higher emission rates were only statistically significant while the vehicles were operated on E0. The calculated fuel consumption was significantly lower for the GDI by 20-22% when compared to the PFI vehicle. Corresponding decreases in CO_2 were also observed. There were no statistically significant changes in the TPM emission rates between the two vehicles.



(a) CO (b) NO$_X$



(c) THC (d) TPM

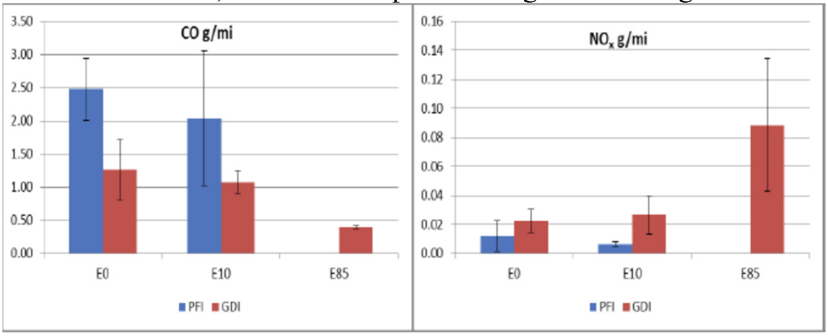


(e) Fuel Consumption (f) CO$_2$

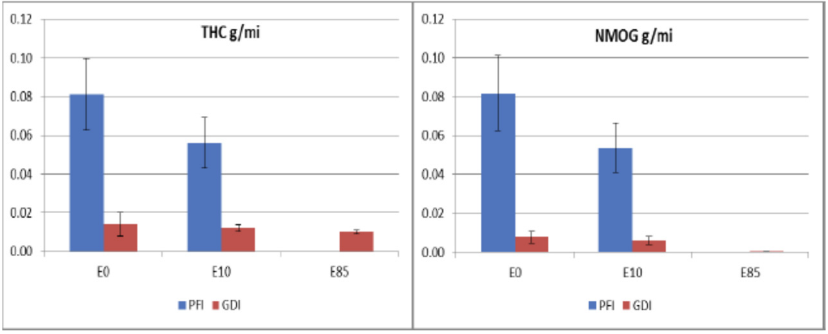
Figure 5.8. Regulated emissions and fuel consumption results of HWFCT cycle

5.1.3 Test results of US06 cycle

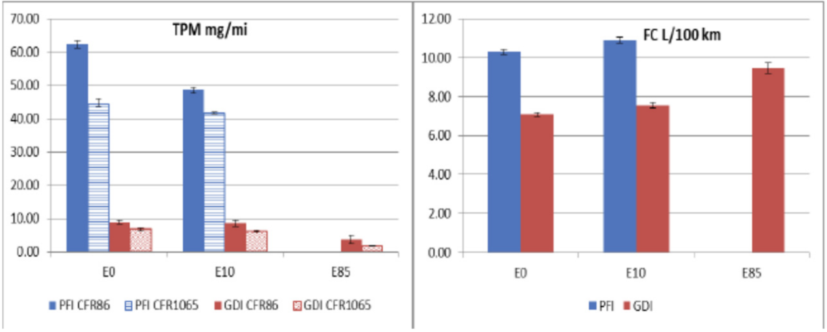
Figure 5.9 and 5.10 shows the test results of two vehicles (PFI and GDI) during the US06 cycle at normal temperature, including regulated emissions, fuel consumption and greenhouse gases.



(a) CO (b) NO_X

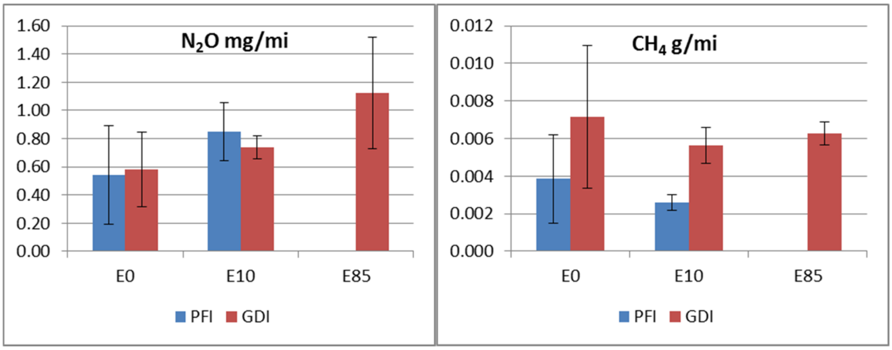


(c) THC (d) NMOG

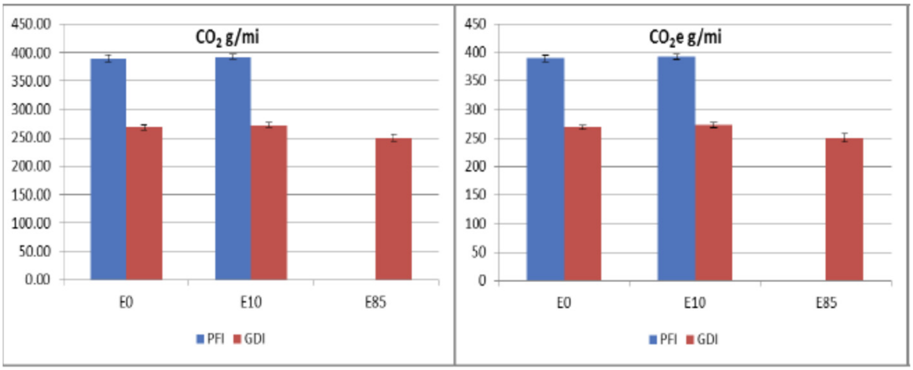


(e) TPM (f) Fuel Consumption

Figure 5.9. Regulated emissions and fuel consumption results of US06 cycle



(a) N_2O (b) CH_4



(c) CO_2 (d) CO_2e

Figure 5.10. Greenhouse gases results of US06 cycle

As seen in Figure 5.9 and 5.10, the emissions results of E10 and E85 fuels during the US06 cycle were compared to those of E0. The impacts of E10 were minimal over the US06. There was a 34% decrease in the calculated NMOG emission rate for the PFI which is due mainly to the decrease in THC and NMHC (-34% not reported in this study). The use of the E10 fuel also resulted in a fuel consumption penalty of 6%-7% for the PFI and GDI respectively. Reductions in CO, NMOG, and TPM ranging from 60% to almost 100% were observed when the GDI was operated on E85. Once again there was a fuel consumption penalty as with the other two drive cycles but a reduction in the CO_2 and overall CO_2e GHG emission rates of 7%. Figure 5.9 and 5.10 also shows the comparison of emissions results between PFI and GDI vehicles during the US06 cycle. Emission rates of CO, NO_X, and NMOG were significantly lower, by 49% to 90%, for the GDI vehicle as compared to the PFI. There was a fuel consumption penalty of 31% for the PFI versus the GDI vehicle. The CO_2 emission rates of the GDI were 31% lower than those of the PFI. This CO_2 decrease led to equally low CO_2e emissions rates. There was a statistically significant increase in the CH_4 emission rate of almost 118% for the GDI compared to the PFI while the vehicles were operated on E10, although there were no differences in N_2O, the remaining measured GHG. Contrary to the observation made over the FTP-75 at 22°C, the GDI had lower TPM emission rates by 82% to 86% for E0 and E10 respectively.

5.2 Finland

5.2.1 CO and HC emissions

CO and HC emissions were higher at -7°C than at +23°C in the cold start NEDC test, particularly for the MPI car (Figure 5.11). Relatively low CO and HC emissions were seen over the hot start FTP75 test at both temperatures, though some differences were observed between cars. CO emission was higher for the MPI car than for the DISI car. The CO emission was generally lower for E85 than for E10 with cars, temperatures and test cycles. E100, however, showed similar or elevated CO emission when compared with E10 or E85 fuels at +23°C.

HC emissions were elevated with the E85 and E100 fuels when compared to E10. Analysis method for total “HC” accounts carbonyl emissions in addition to hydrocarbons.

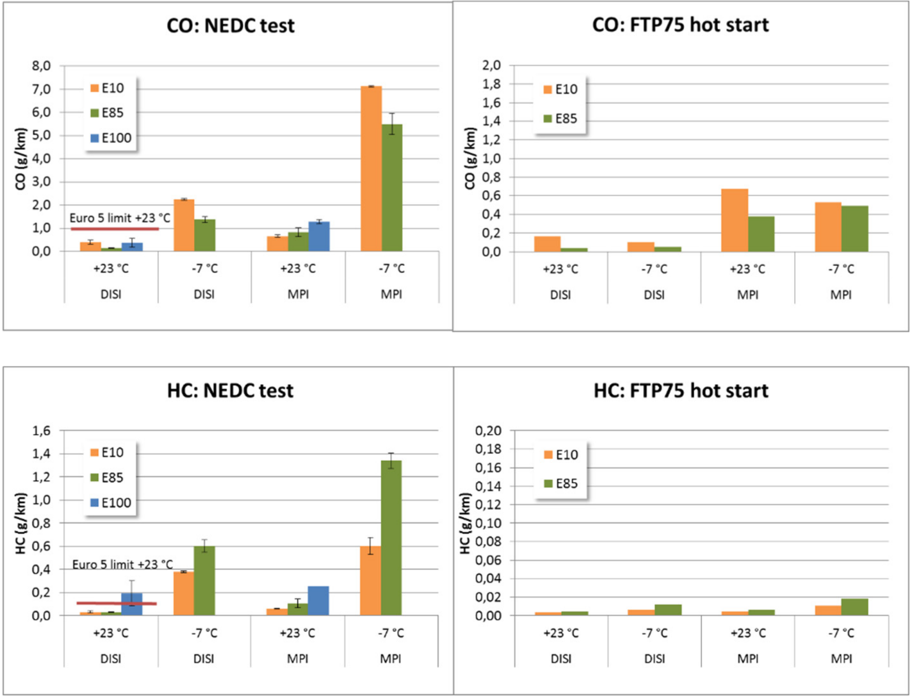


Figure 5.11. CO and HC emissions over cold-start NEDC and hot-start FTP75 test cycles.

Individual C1-C8 hydrocarbons were considerably higher at -7°C than at +23°C for both cars over the NEDC test cycle (Figure 5.12). Sum of C1-C8 emissions was generally higher for the MPI car than for the DISI car, particularly at -7°C.

For E85 at +23°C, the main C1-C8 compounds present were methane, and to lesser extent ethene, xylenes and acetylene. The overall C1-C8 emissions were higher for E100 than for E85 at +23°C. For E10, the sum of C1-C8 emissions were at the same level as those for the E85 fuel, but the composition was different. For E10 the predominant compounds observed were aromatics (toluene, xylenes), and to lesser extent ethene and methane.

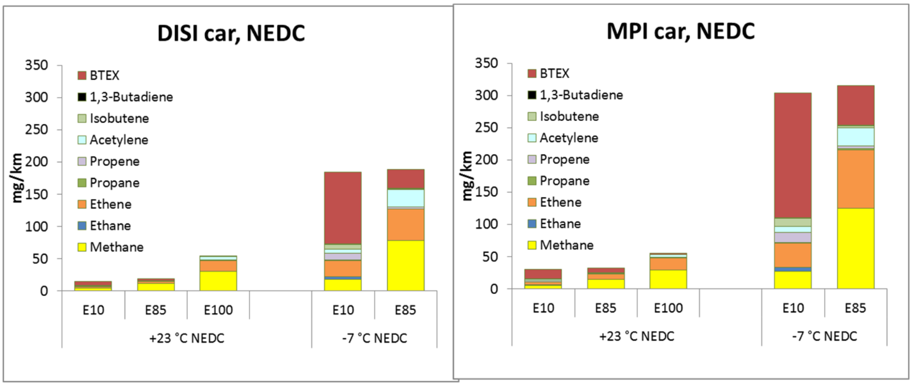


Figure 5.12. C1-C8 hydrocarbon emissions over the cold-start NEDC test.

5.2.2 Ethanol and aldehyde emissions

An overview of the selected unregulated emissions is shown in Figure 5.13. In the European test cycle aldehydes and speciated hydrocarbons were measured with HPLC and GC methods, whereas less accurate FTIR technology was used for these emission species in the FTP75 test cycle. Therefore an overview given in Figure 5.13 is indicative for the FTP75 tests. Alcohols were measured only by FTIR in all tests.

Alcohol emissions, primarily ethanol, dominated for the E85 and E100 fuels in the cold-start NEDC test. Particularly high ethanol emissions were seen in the NEDC test at -7°C for the E85 fuel. An ethanol emission of 1.5 g/km over NEDC at -7°C would mean that around 2.1% of E85 fuel consumption ends up as unburnt exhaust ethanol (assuming 70 g/km fuel consumption). For E100, ethanol emissions were substantial at +23°C. It is noticeable that ethanol emissions were very low for E85 and E100 in the hot-start FTP75 test at both test temperatures.

Acetaldehyde is the second highest emission after ethanol emission for the E85 and E100 fuels. Acetaldehyde emissions increased dramatically with higher fuel ethanol content, particularly at low test temperature with the MPI car (Figure 5.14). Generally, formaldehyde and acetaldehyde emissions were higher for the E85 and E100 fuels than for the E10 fuel in the cold-start NEDC test. In the hot-start FTP75 test, aldehyde emissions were negligible for both cars and fuels.

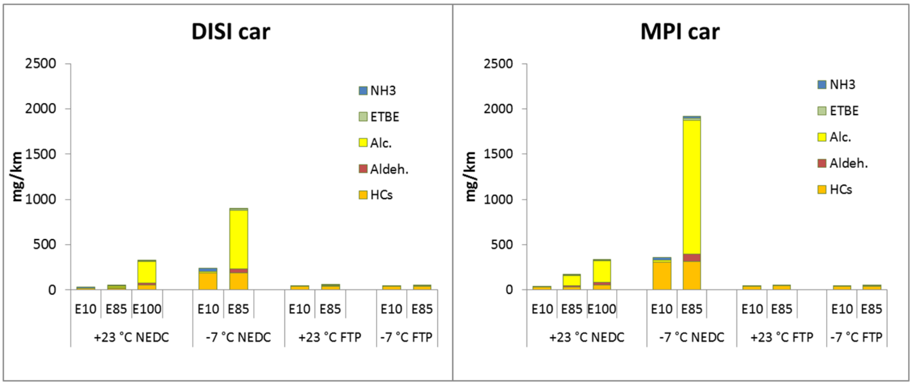


Figure 5.13. Overview of unregulated emissions over the cold-start NEDC test and hot-start FTP75 test.

Formaldehyde emissions from both cars measured were low even when the tightest formaldehyde limit of 4 mg/mi in California for SULEV cars is regarded. The formaldehyde emission was at the highest level for the DISI car when using E85 fuel at -7°C, namely 4.5 mg/km.

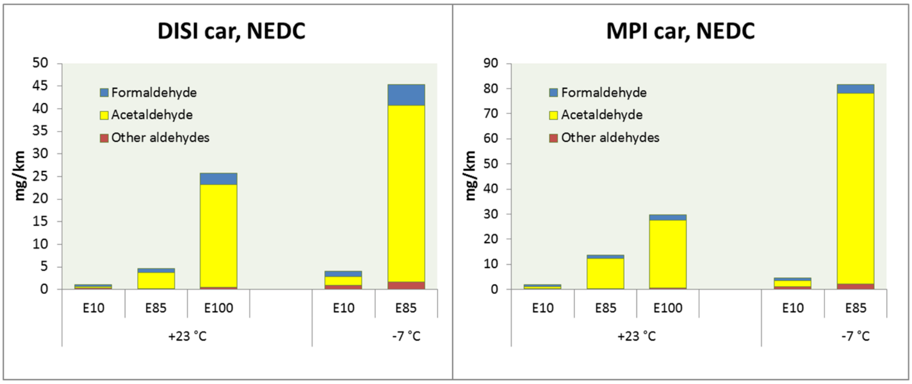


Figure 5.14. Formaldehyde and acetaldehyde emissions over the cold-start NEDC test.

Acetaldehyde emission was observed in substantial concentrations over 3 minutes after the cold-start of car at -7°C (Figure 5.15). At +23°C test temperature acetaldehyde emission peaked over much shorter period after the start of the car. Formaldehyde emission was seen in significant concentrations only in the beginning of the test.

5.2.3 NO_X, ammonia and nitrous oxide

The NO_X emissions were relatively low over the cold-start NEDC test, even though elevated emissions were observed for the DISI car at -7°C (Figure 5.16). Only small differences in NO_X emissions between fuels were detected for the DISI car over the NEDC test. With the MPI car, slightly elevated NO_X emissions were observed for the E85 fuel, but not for the E100 fuel.

Over the hot start FTP75 test, the NO_X emission level was surprisingly high. NO_X emission for the MPI car with E85 was 228 mg/km at +23°C and 139 mg/km at -7°C. NO_X emission for the DISI car at -7°C was up to 343 mg/km. High NO_X emissions were not expected in the hot-start test with warmed-up engine. In addition, higher NO_X emissions for the E85 fuel than for the E10 fuel was unexpected.

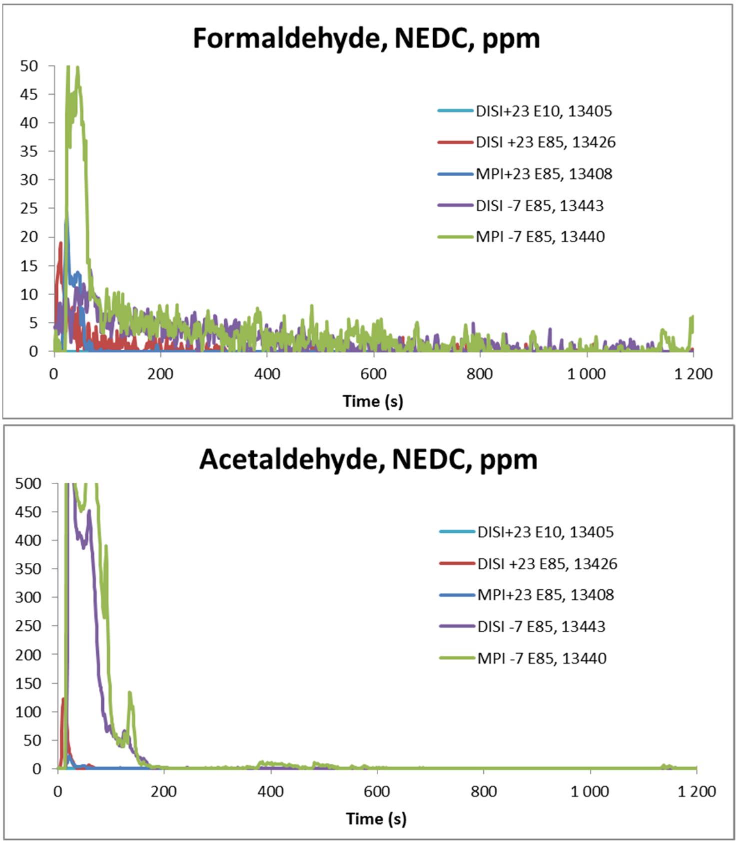


Figure 5.15. Formaldehyde and acetaldehyde emissions over the NEDC test.

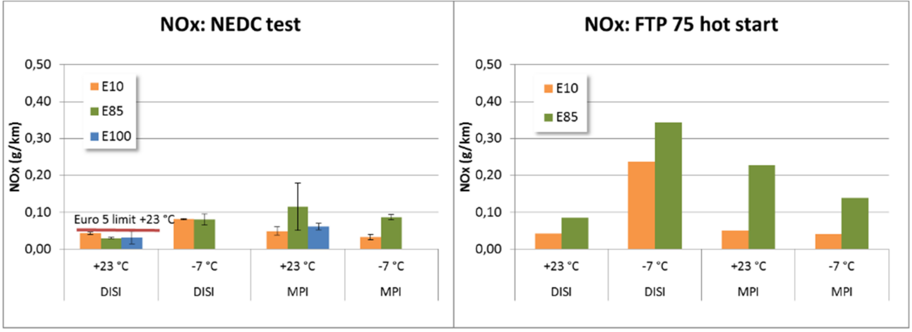


Figure 5.16. NO_X emission over cold-start NEDC and FTP75 test cycles.

Figure 5.17 shows NO_X concentration with DISI and MPI cars over the cold-start NEDC and hot-start FTP75 tests at -7°C. In the NEDC test, NO_X was emitted in the beginning of test after the cold start and during accelerations. In the hot-start FTP test, high NO_X concentrations were observed in the accelerations, however, the highest emissions were seen after a 10 minutes pause. This indicates that these engines may be optimised for low CO and HC emissions leading to conditions that are not favourable for reduction of NO_X in the TWC due to possibly lean air-to-fuel ratio.

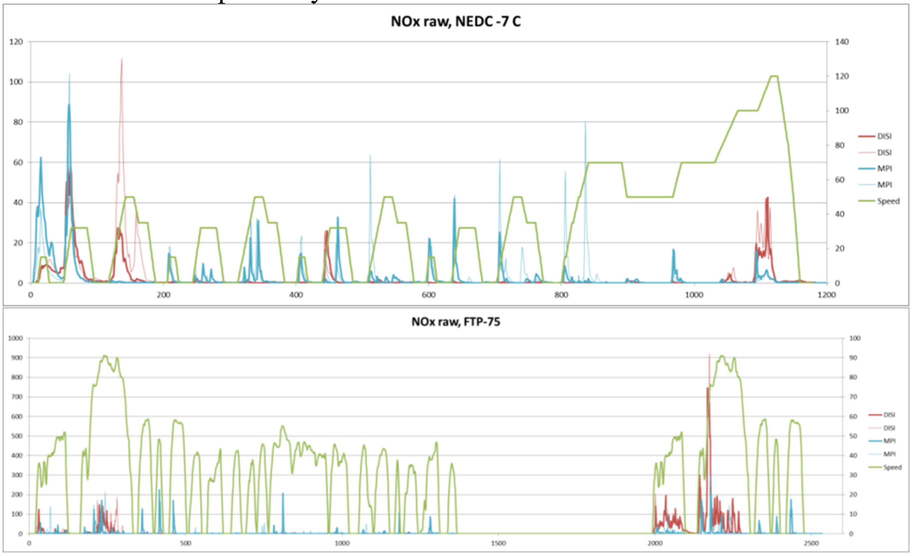


Figure 5.17. NO_X emissions in the NEDC and hot-start FTP test.

Ammonia, nitrous oxide and nitrogen dioxide emissions are shown in Figure 5.18. Ammonia is induced by the three-way catalysts of the spark-ignited cars, as well as nitrous oxide emission. Some aftertreatment devices, such as diesel particle filters, enhance formation of nitrogen dioxide.

Nitrogen dioxide emissions were low below 3 mg/km. Nitrous oxide emissions were also low, below 5 mg/km. Both of these emissions were practically below the detection limit of the FTIR method, whereas ammonia emission clearly exceeded the detection limit.

Ammonia emission was higher at -7°C than at +23°C in the cold-start NEDC test. The hot start FTP75 test at both temperatures showed similar level of ammonia emission as the NEDC test at +23°C. MPI and DISI cars emitted quite similar emission levels of ammonia. The highest single emission result, close to 50 mg/km, was obtained for the E10 fuel with the DISI car over the NEDC test cycle at -7°C.

Ammonia concentrations are presented in Figure 5.19. Ammonia concentrations were high in general, exceeding 10 ppm in major part of tests. In addition, substantial peaks up to 300-500 ppm were observed. These ammonia concentrations are high when compared to limit value of 10 ppm for SCR equipped heavy-duty engines, for example.

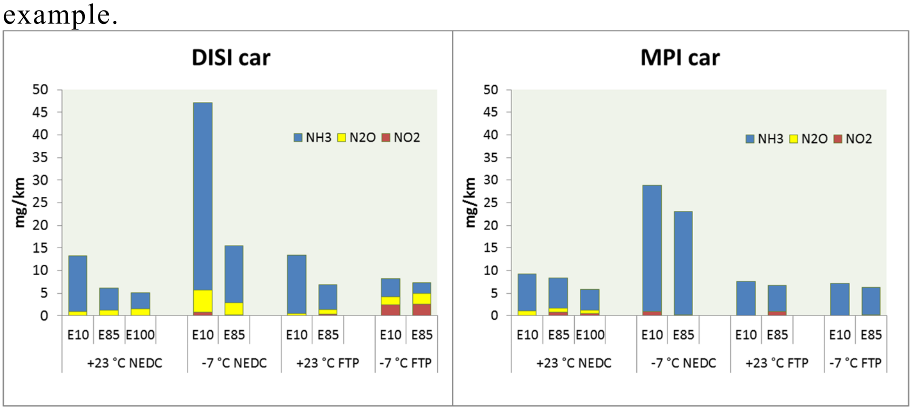


Figure 5.18. Ammonia, nitrous oxide and nitrogen dioxide emissions over the cold-start NEDC and hot-start FTP75 driving cycles.

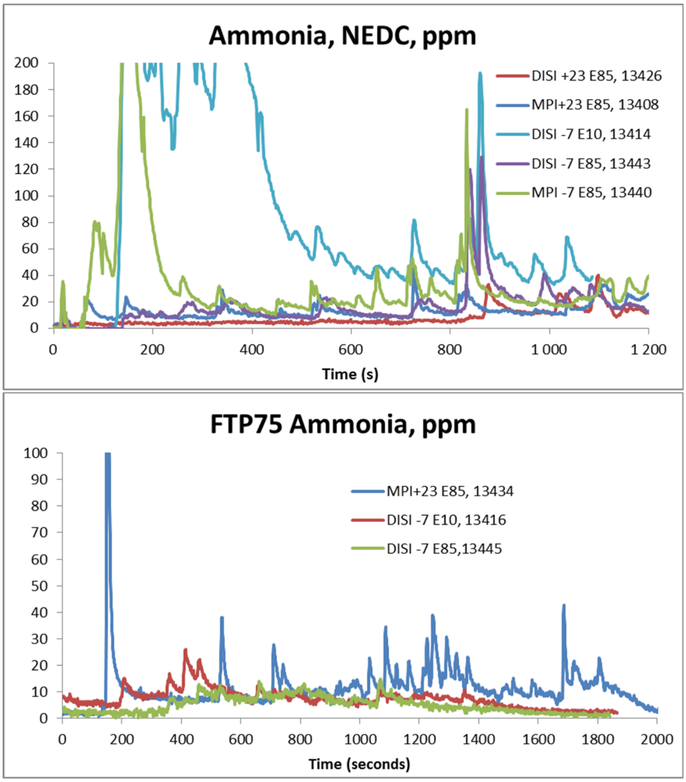


Figure 5.19. Ammonia concentrations over the selected tests.

Ammonia concentrations in Figure 5.19 are not carefully adjusted with the test cycle, and therefore the test cycle dependence cannot be analysed. However, slight correlations between ammonia formation and the test cycle could be present. In theory, ammonia formation is enhanced in slightly rich air-to-fuel ratio at high temperatures (aggressive accelerations) when sufficiently HC and NO_X emissions are present (Li et al. 2010, Mejia-Centeno 2007, Heeb et al. 2006). Engine-out emissions were not measured in this project, but it is assumed that HC and NO_X are not a limiting condition for ammonia formation in these tests.

5.2.4 Particle mass and number emissions

Particulate matter emissions (PM) were generally low (i.e. below 7 mg/km) in all cases, however, higher PM were observed at -7°C than at +23°C (Figure 5.20). By default, PM emissions decrease with increasing ethanol content of the fuel, and this was also the case in these tests. PM emissions were extremely low over the hot-start FTP75 test (below 1 mg/km) for both fuels and cars tested.

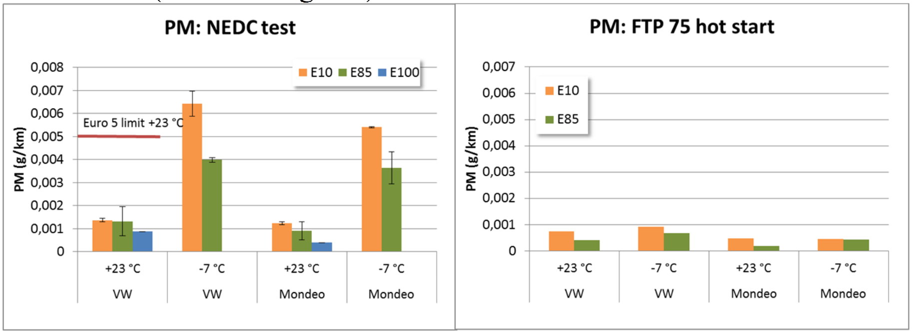


Figure 5.20. PM emission over the cold-start NEDC and the hot-start FTP75 driving cycles.

“Wet” particle number emissions (PN) were higher for E10 than for E85 over the NEDC test (Figure 5.21). So, E85 reduced particle number emissions effectively for both cars. PN results for E100 were extremely low. PN was relatively low for both cars over the hot-start FTP75 test. The “wet” particle number results here cannot be compared with the limit values of the Euro 5/6 emission regulation, which takes into account only solid “dry” particles (volatile portion evaporated).

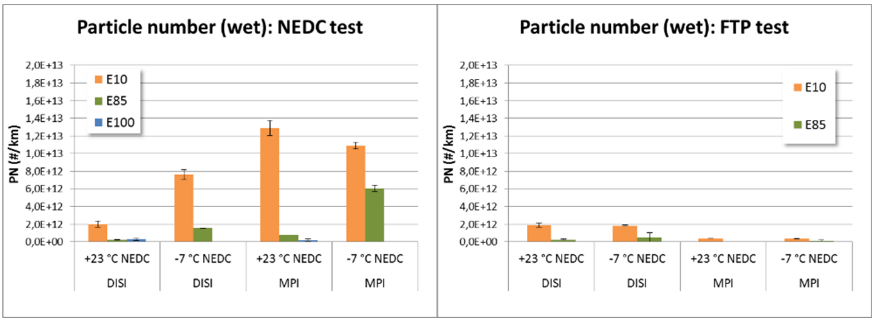


Figure 5.21. “Wet” particle number results.

Nucleation tendency was observed for the MPI car, which was seen also in high total wet PN results (Figure 5.22). Nucleation tendency was particularly strong when using E10 fuel. Accumulation mode particles dominated for the DISI car.

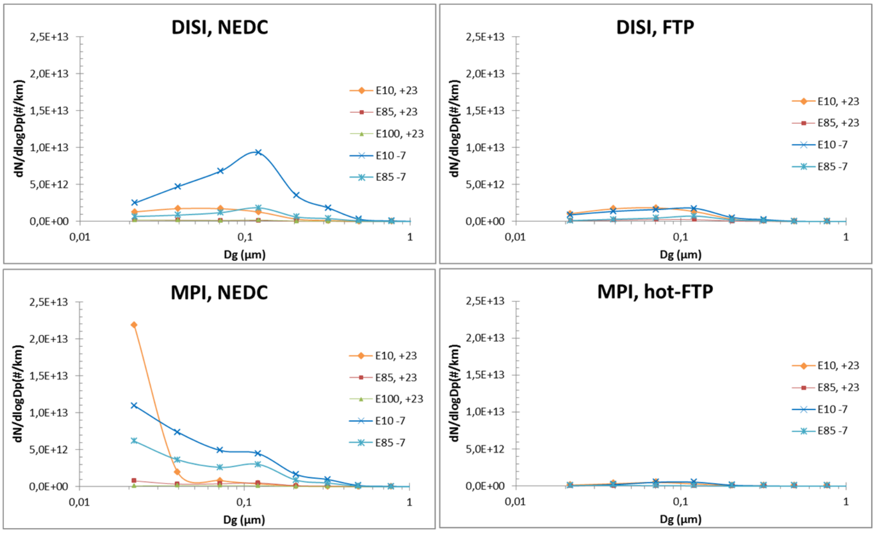


Figure 5.22. “Wet” particle number size distribution results.

Figure 5.23 shows driving cycle dependence of particles of two particle size classes, Da 21.5 nm and Da 71.3 nm. For the MPI car, particles in these size classes were formed in the accelerations and in the high-speed part of the NEDC test, whereas for the DISI car particles were concentrated in the accelerations.

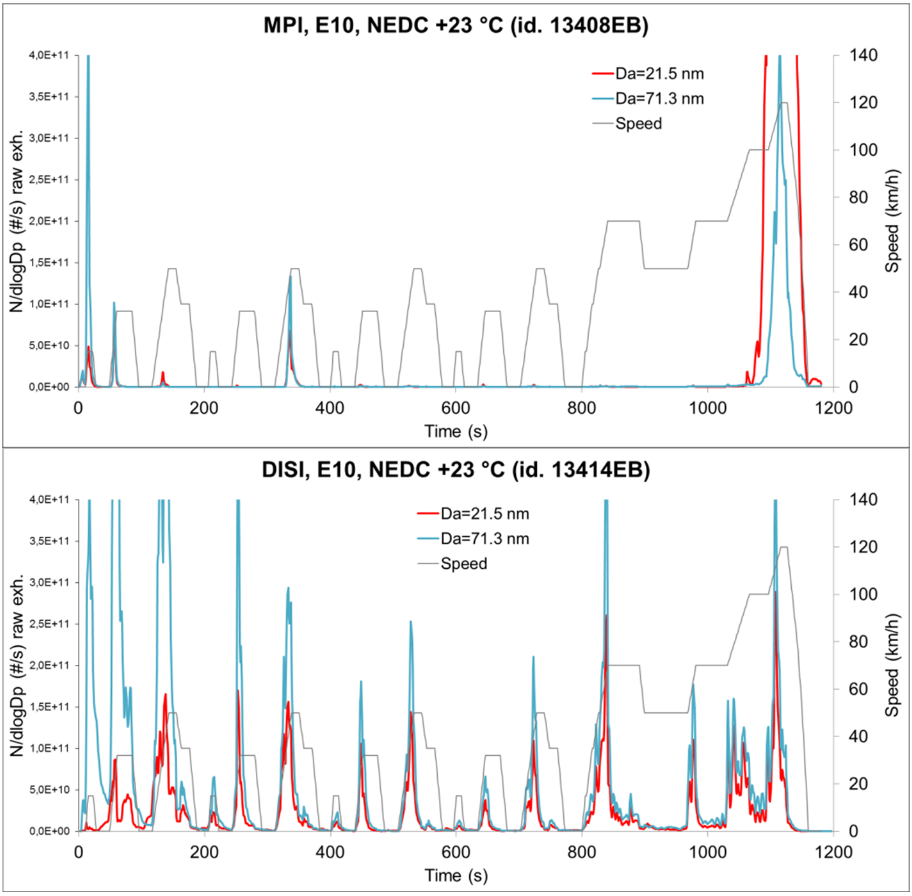
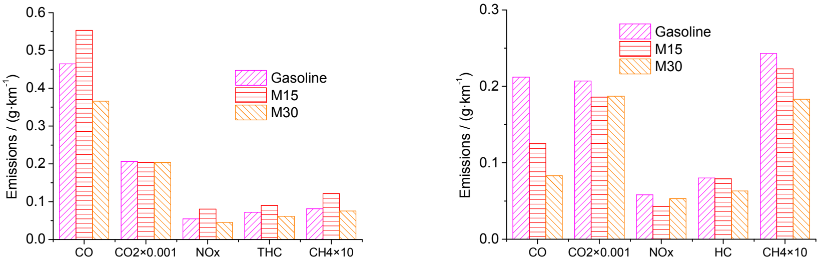


Figure 5.23. "Wet" particle number emissions at size classes of Da 21.5 nm and 71.3 nm for MPI and DISI cars over the cold-start NEDC test.

5.3 China

5.3.1 Vehicle exhaust emissions at ambient temperature

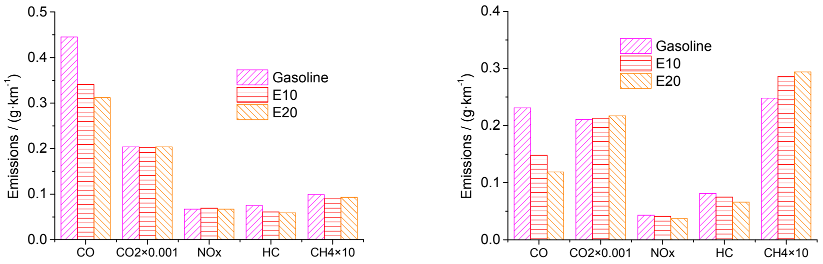
Cycle Average Regulated Emissions. Figure 5.24 shows the cycle average regulated emissions of gasoline, M15, and M30 three fuels of two vehicles (PFI and GDI). Figure 5.25 shows the cycle average regulated emissions of gasoline, E10, and E20 three fuels of two vehicles (PFI and GDI). The average values of the MEXA analysis results of bag sampling, integral results of MEXA instantaneous values, and integral results of FTIR instantaneous values are defined as the measurement results of CO, NO_X, and CO_2 emissions. The average values of the MEXA analysis results of bag sampling and integral results of MEXA instantaneous values are defined as the measurement results of HC emissions. The average values of the MEXA analysis results of bag sampling and integral results of FTIR instantaneous values are defined as the measurement results of CH_4 emissions.



(a) PFI vehicle (b) GDI vehicle

Figure 5.24. Effects of methanol proportions in fuels on cycle average regulated emissions

Seeing from Figure 5.24(a), CO_2 emissions of gasoline, M15, and M30 fuels remain basically unchanged. CO, NO_X, HC, and CH_4 emissions of M15 fuel are higher than those of gasoline. Oppositely, those emissions of M30 fuel are lower than those of gasoline. Blending methanol with gasoline fuels will cause the air-fuel mixture becoming too lean, especially in the beginning stage of the engine cold start. It is easy to make a misfire, resulting in increasing CO and HC emissions. However, the oxygen content of methanol will promote the complete combustion of the fuel, causing a downward trend of CO and HC emissions. As low proportional methanol blending in gasoline fuels, the varying trends of CO, HC, NO_X, and CH_4 emissions are affected by the calibration of the engine cold start, which do not show a monotonous increase or decrease. As the low calorific value of methanol is lower than that of gasoline, the fuel consumption of methanol gasoline fuel is greater than that of gasoline. However, the hydrocarbon ratio of methanol is less than that of gasoline. These two contrary influencing factors cause that CO_2 emissions of gasoline, M15, and M30 fuels are basically the same. It indicates that the effective efficiency of vehicles fuelled with low proportion of methanol gasoline fuels is consistent with those of gasoline. Figure 5.24(b) shows that for GDI vehicle CO emissions decrease and CO_2 emissions remain basically the same with the increase of methanol proportions in fuels.

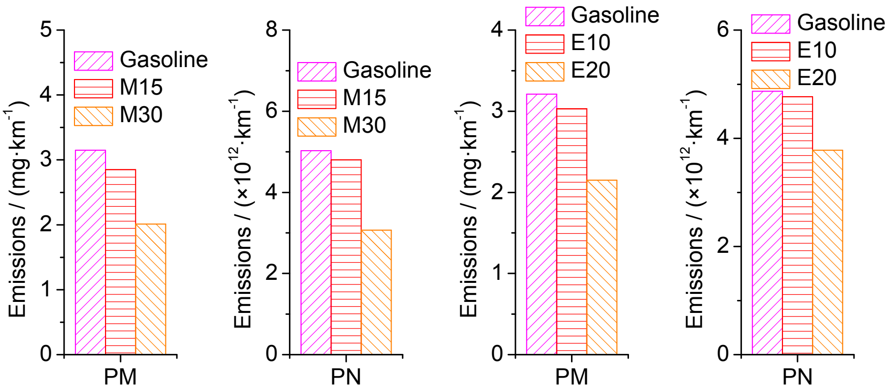


(a) PFI vehicle (b) GDI vehicle

Figure 5.25. Effects of ethanol proportions in fuels on cycle average regulated emissions

Shown in Figure 5.25(a), CO_2 and NO_X emissions of gasoline, E10, and E20 fuels are basically the same. CO, HC, and CH_4 emissions decrease with the increasing ethanol proportions in fuels. The test results indicate that the oxygen content of ethanol will promote the adequate combustion of fuels, resulting in effectively reducing the generation of CO, HC, and CH_4 emissions. However, the generation of NO_X is less affected by the ethanol content. Furthermore, as the lower calorific value of ethanol is approximately 60% of that of gasoline, the fuel consumption of the entire NEDC are in the order of E20 > E10 > gasoline. However, the carbon mass content of ethanol is 60% of that of gasoline. The CO_2 emissions generated from the same fuel consumption are in the same order of E20 < E10 < gasoline. These two opposing influencing factors cause that the results of CO_2 emissions are basically the same. Figure 5.25(b) shows that for GDI vehicle CO emissions decrease and CO_2 emissions remain basically the same with the increase of ethanol proportions in fuels, which has the similar characteristics as methanol fuels.

Figure 5.26 gives the effects of methanol and ethanol content in fuels on cycle average particulate emissions (only GDI vehicle), including particulate mass (PM) and particulate number (PN). The results show that PM and PN emissions in vehicle exhaust decrease proportionally as the increase of methanol and ethanol content in fuels. The reason is that the oxygen content of methanol and ethanol in fuels is helpful for the complete oxidation of particulate emission.

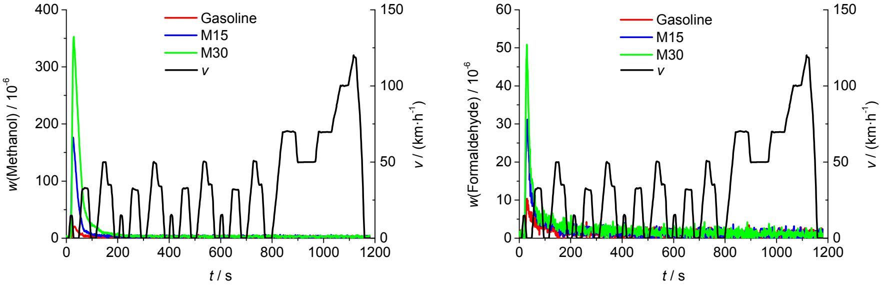


(a) methanol fuels (b) ethanol fuels

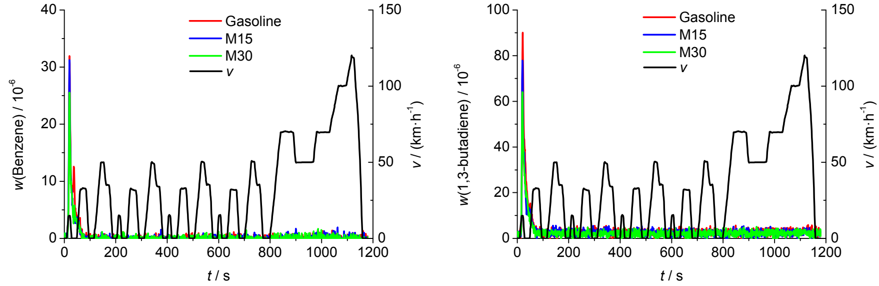
Figure 5.26. Effects of alcohol proportions in fuels on cycle average particulate emissions

Instantaneous Unregulated Emissions. Figure 5.27(a)~(d) gives the instantaneous emissions curves of methanol, formaldehyde, benzene, and 1,3-butadiene of gasoline, M15, and M30 fuels during the entire NEDC. The effects of ethanol proportions in gasoline, E10 and E20 three fuels on the instantaneous emissions of acetaldehyde, toluene, propylene, and 1,3-butadiene are researched, as shown in Figure 5.28(a)~(d).

Seeing from Figure 5.27 and Figure 5.28, the instantaneous emissions curves of methanol, formaldehyde, acetaldehyde, benzene, toluene, propylene, and 1,3-butadiene were similar. During the curves, the highest instantaneous peak occurred in the first accelerating conditions at the beginning of the cold start. The emissions gradually reduced to nearly zero at about 100s, and then maintained zero-emission level until the end of the NEDC. The measurement results indicate that methanol, formaldehyde, acetaldehyde, benzene, toluene, propylene, 1,3-butadiene emissions could be converted completely by the three-way catalyst and the vehicle-out emissions after the catalyst remain in a rather low level, as those pollutants are essentially hydrocarbons. Overall, vehicle unregulated emissions during the entire NEDC mainly depended on the first 100s of the cold start before the catalyst completely lighted off.



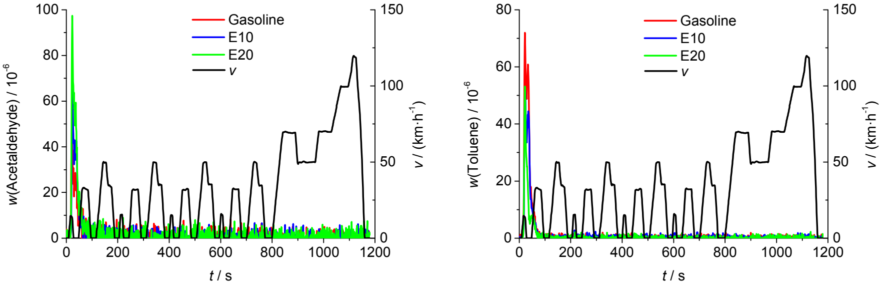
(a) Methanol (b) Formaldehyde



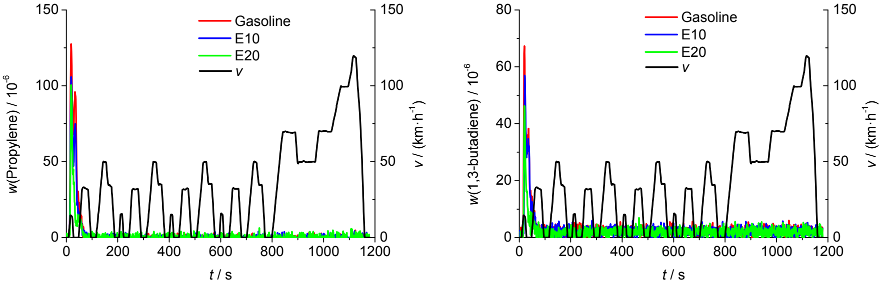
(c) Benzene (d) 1,3-butadiene

Figure 5.27. Instantaneous emissions curves of unregulated pollutants of different proportional methanol fuels

Shown in Figure 5.27(a), the peak values of methanol emissions in the vehicle exhaust increased proportionally, as the increase of methanol proportions in gasoline fuels. The first methanol emission peak of M30 was as high as 350×10^{-6}. At the same time the methanol peak value of M15 was 180×10^{-6} while that of gasoline was about 35×10^{-6}. Seeing from Figure 5.27(b), formaldehyde emissions were obviously less than methanol emissions, as formaldehyde was the intermediate product in the combustion of methanol. Formaldehyde emissions of M30, M15, and gasoline fuels gradually decreased, which were respectively 50×10^{-6}, 30×10^{-6}, and 10×10^{-6}.



(a) Acetaldehyde (b) Toluene



(c) Propylene (d) 1,3-butadiene

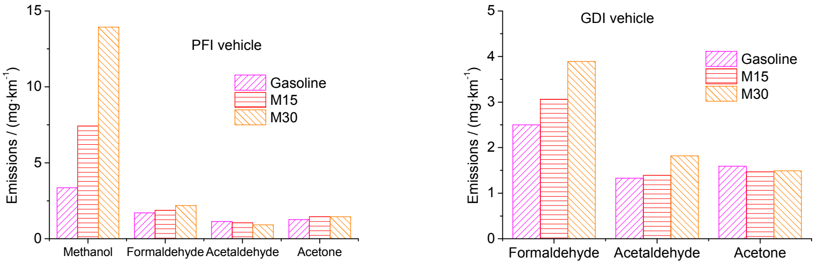
Figure 5.28. Instantaneous emissions curves of unregulated pollutants of different proportional ethanol fuels

In Figure 5.27(c)~(d), benzene and 1,3-butadiene instantaneous emissions curves of different proportional methanol gasoline fuels also showed the stepped distribution. The peak values of benzene and 1,3-butadiene instantaneous emissions of gasoline, M15, and M30 fuels decreased slightly with the increase of the methanol content in fuels.

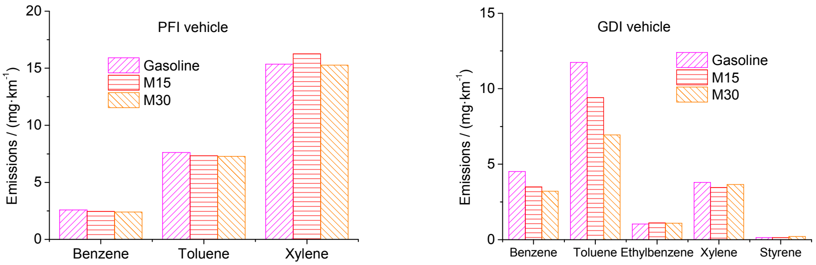
Seeing from Figure 5.28(a), the instantaneous acetaldehyde emissions had an obvious stepped increase, as the ethanol content increasing in gasoline, E10 and E20 three fuels. Shown in Figure 5.28 (a), there were two obvious peaks of acetaldehyde instantaneous emissions of E20, which were 100×10^{-6} and 60×10^{-6}. The reason is that, the fuel enrichment at the accelerating conditions caused the incomplete combustion of the ethanol content in fuels and generated a large amount of acetaldehyde emissions. The acetaldehyde instantaneous emissions of E10 also had two peaks at the same point. However, the peak values reduced to 70×10^{-6} and 40×10^{-6}. The emissions peaks of gasoline were lowest at the same time, which were only about 45×10^{-6} and 25×10^{-6}.

Shown in Figure 5.28 (b)~(d), toluene, propylene, and 1,3-butadiene instantaneous emissions curves also showed a clear stepped distribution, which was different with those of acetaldehyde emissions. Those emissions decreased oppositely with the increase of the ethanol content in fuels. Seeing from Figure 5.28 (b)~(d), toluene, propylene, and 1,3-butadiene instantaneous emissions of gasoline and E10 fuels both had two peaks at the first 100s during the cold start. However, those emissions of E20 fuel only had the first peak, while the peak values clearly reduced.

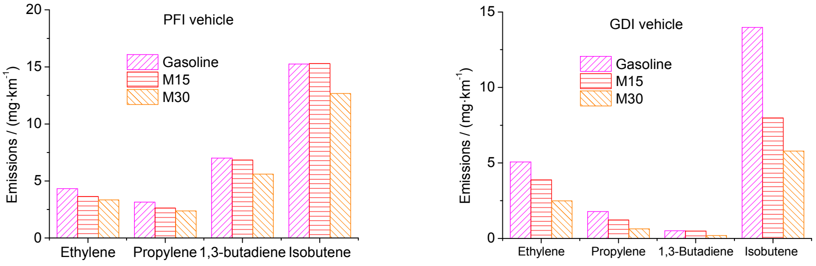
Cycle Average Unregulated Emissions. Figure 5.29 shows the cycle average key unregulated emissions of gasoline, M15, and M30 three fuels of two vehicles (PFI and GDI). Figure 5.30 shows the cycle average key unregulated emissions of gasoline, E10, and E20 three fuels of two vehicles (PFI and GDI). The unregulated pollutants include alcohols, aldehydes, ketones, aromatic hydrocarbons, and olefins. The average values of the chemical analysis results of bag sampling and integral results of FTIR instantaneous values are defined as the measurement results of formaldehyde, acetaldehyde, benzene, and toluene emissions. The chemical analysis results of bag sampling are defined as the measurement results of acetone and xylene emissions. The integral results of FTIR instantaneous values are defined as the measurement results of methanol, ethylene, propylene, 1,3-butadiene, and isobutene emissions.



(a) Alcohols, aldehydes and ketones



(b) Aromatic hydrocarbons

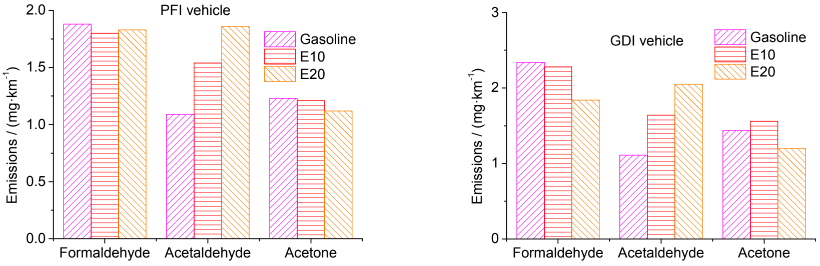


(c) Olefins

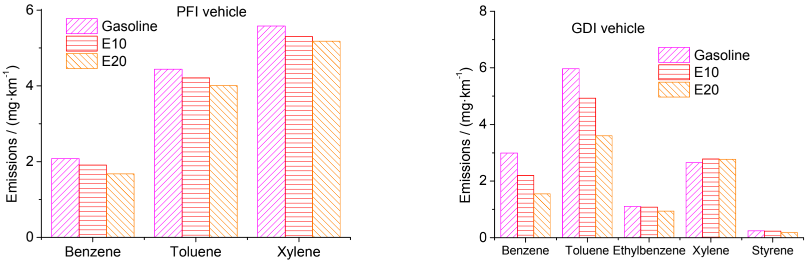
Figure 5.29. Effects of methanol proportions in fuels on cycle average unregulated emissions

Firstly, the effects of methanol content in fuels on PFI vehicle exhaust emissions are analyzed. Seeing from Figure 5.29(a), as the increase of the methanol proportions in fuels, methanol and formaldehyde emissions increase proportionally, while acetaldehyde and acetone emissions remain basically the same. The methanol emission of M30 is 415% of that of gasoline, while M15 is 221% of gasoline. Besides, formaldehyde emissions of M30 and M15 are respectively 128% and 110% of that of gasoline. Figure 5.29(b) shows that benzene and toluene emissions decrease as the increase of the methanol content in fuels, while the variation is slight. The xylene emissions of three fuels are basically the same. The benzene emission of M30 is 93.6% of that of gasoline, while M15 is 95.6% of gasoline. The toluene emissions of M30 and M15 are 95.6% and 96.3% of that of gasoline. Figure 5.29(c) shows that the ethylene, propylene, 1,3-butadiene, and isobutene emissions decrease with the increasing methanol proportion in the fuel.

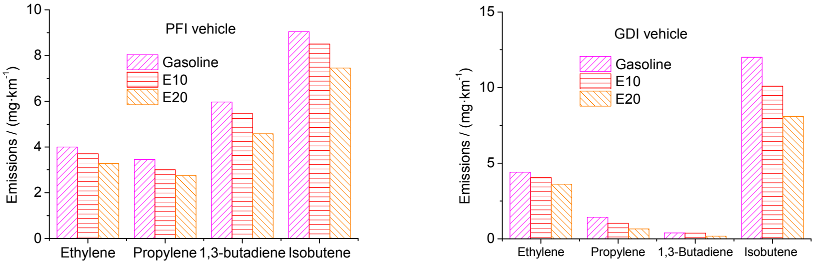
Secondly, GDI vehicle exhaust emissions have a similar characteristic varying with methanol proportions in fuels. Formaldehyde emissions of M30 and M15 are respectively 156.0% and 122.7% of that of gasoline. The benzene emission of M30 is 71.2% of that of gasoline, while M15 is 77.7% of gasoline. The toluene emissions of M30 and M15 are 59.1% and 80.1% of that of gasoline. Ethylene, propylene, 1,3-butadiene, and isobutene emissions decrease with the increasing methanol proportion in the fuel.



(a) Aldehydes and ketones



(b) Aromatic hydrocarbons



(c) Olefins

Figure 5.30. Effects of ethanol proportions in fuels on cycle average unregulated emissions

The influences of different ethanol content in fuels on PFI vehicle exhaust emissions were compared. Shown in Figure 5.30(a), acetaldehyde emissions increase proportionally with the increase of the ethanol content in fuels. Acetaldehyde emissions of E20 and E10 fuels are 171.2% and 142.2% of that of gasoline. This is consistent with the results of acetaldehyde instantaneous emissions. The measurement results indicate that the incomplete oxidation of ethanol fuel will cause the generation of a large amount of acetaldehyde emissions in the vehicle exhaust. Formaldehyde and acetone emissions are nearly independent of the effects of the ethanol proportions in fuels. Seeing from Figure 5.30(b), benzene and toluene emissions decrease proportionally with the increase of the ethanol proportion in fuels. Xylene emissions of gasoline, E10, and E20 three fuels also gradually reduce while the variation is slight. The benzene emission of E20 is 81.0% of that of gasoline, while E10 is 92.1% of gasoline. The toluene emissions of E20 and E10 are about 90.4% and 94.8% of that of gasoline. The trend is the same as instantaneous toluene emissions of three fuels. The xylene emissions of E20 and E10 are approximately 93.0% and 95.0% of that of gasoline. The measurement results indicate that blending ethanol with gasoline fuels could reduce benzene, toluene, and xylene emissions in the vehicle exhaust in a certain extent, as ethanol does not have the aromatic hydrocarbon content. Shown in Figure 5.30(c), ethylene, propylene, 1,3-butadiene, and isobutylene emissions decrease nearly linearly with the increase of the ethanol content in fuels. The ethylene emission of E20 is 82.1% of that of gasoline, while E10 is 92.8% of gasoline. The propylene emissions of E20 and E10 are about 80.1% and 87.3% of that of gasoline, while the 1,3-butadiene emissions of E20 and E10 are 76.6% and 91.4% of that of gasoline. This is consistent with the instantaneous results of propylene and 1,3-butadiene emissions. The isobutylene emissions of E20 and E10 are about 82.4% and 94.0% of that of gasoline. The measurement results indicate the oxygen content of ethanol in fuels is helpful for the complete oxidation of olefins in fuels, which could effectively reduce the olefin emissions in the vehicle exhaust.

The influences of ethanol content in fuels on GDI vehicle exhaust unregulated emissions were also analyzed. Acetaldehyde emissions of E20 and E10 fuels are 183.9% and 146.9% of that of gasoline. The benzene emission of E20 is 73.7% of that of gasoline, while E10 is 82.5% of gasoline. The toluene emissions of E20 and E10 are about 51.8% and 60.3% of that of gasoline. Ethylene, propylene, 1,3-butadiene, and isobutylene emissions decrease with the increase of the ethanol. The ethylene emission of E20 is 81.8% of that of gasoline, while E10 is 91.7% of gasoline.

5.3.2 Vehicle exhaust emissions at low temperature

In accordance with the EU R83-05 standard, emissions testing at the -7°C low temperature of the NEDC were carried out in a light-duty vehicle chassis dynamometer, using vehicle 1# fuelled with gasoline, M15, M30 and using vehicle 2# fuelled with gasoline, E10, E20. The effects of methanol and ethanol proportions in fuels on CO, NO_X, HC, CO_2 regulated emissions and methanol, formaldehyde, acetaldehyde, acetone, benzene, toluene, xylene, ethylene, propylene, 1,3-butadiene, isobutylene unregulated emissions were analyzed using FTIR, HPLC and GC-MS joint research methods. The variations of different pollutants emissions at low and normal temperature were also compared.

Average regulated emissions at low temperature. Figure 5.31 shows respectively the average regulated emissions of gasoline, M15 and M30 three fuels at low temperature. Figure 5.32 shows respectively the average regulated emissions of gasoline, E10 and E20 three fuels at low temperature. Seen from Figure 5.31, CO2 emissions of gasoline, M15 and M30 three fuels at low temperature are basically the same. CO emissions of M30 and M15 fuels are respectively 125% and 128% of that of gasoline. HC emissions of M30 and M15 fuels are respectively 120% and 105% of that of gasoline. Oppositely, NO_X emissions of the two fuels are 92% and 81% of that of gasoline. Figure 5.32 shows CO_2 emissions of gasoline, E10 and E20 three fuels remain nearly unchanged at low temperature. CO emissions of E20 and E10 fuels are respectively 108% and 98% of that of gasoline, while HC emissions of the two fuels are 102% and 97% of that of gasoline. However, NO_X emissions of E20 and E10 fuels are respectively 83% and 83% of that of gasoline. Comprehensively speaking, when low proportional methanol or ethanol fuels is added into gasoline, CO_2 emissions are basically, CO and HC emissions increases slightly, and the NO_X emissions have a tendency to reduce at low temperature.

As shown in Table 5.1, the comparison results of regulated emissions and unregulated emission of CO, CO_2, NO_X and HC pollutants at low temperature and normal temperature. The test results indicate that all kinds of regulated emissions at low temperature are obviously higher than those at normal temperature. For low proportional methanol-gasoline and ethanol-gasoline fuels, CO_2 emissions at low temperature are 1.7 times as high as those at normal temperature. CO, HC, and NO_X emissions at low temperature are respectively 7~13 times, 25~33 times, 2~5 times as high as those at normal temperature. With the increase of the alcohol content in fuels, the ratios of CO, HC emissions at low temperature to those at normal temperature have a tendency to increase, while NO_X emissions fell slightly.

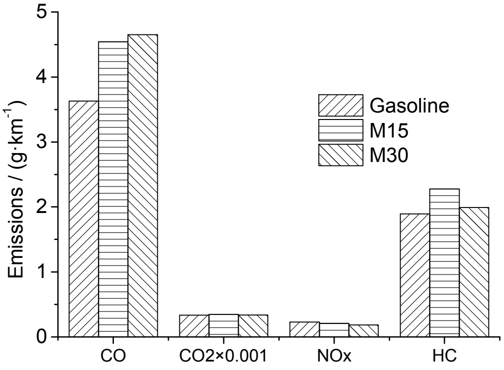


Figure 5.31 Effects of methanol proportions in fuels on cycle average regulated emissions at low temperature

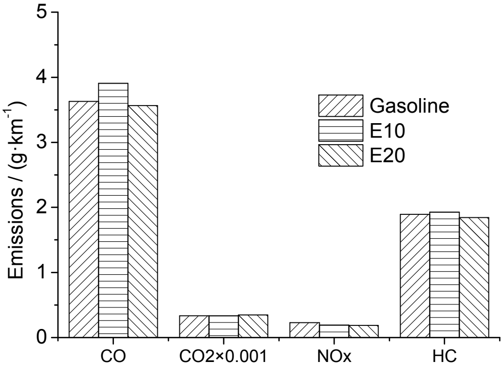


Figure 5.32 Effects of ethanol proportions in fuels on cycle average regulated emissions at low temperature

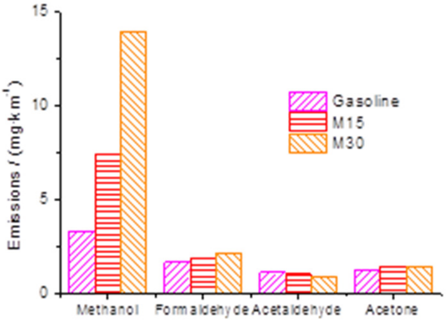
Table 5.1 Comparison of regulated emissions at low temperature and normal temperature

Pollutants	Ratios of methanol fuels			Ratios of ethanol fuels		
	Gasoline	M15	M30	Gasoline	E10	E20
CO	7.8	8.2	12.7	8.1	11.4	11.4
CO_2	1.6	1.7	1.7	1.6	1.7	1.7
NO_X	4.2	2.6	4.0	3.4	2.8	2.8
HC	26.2	25.2	32.5	25.4	31.7	31.1

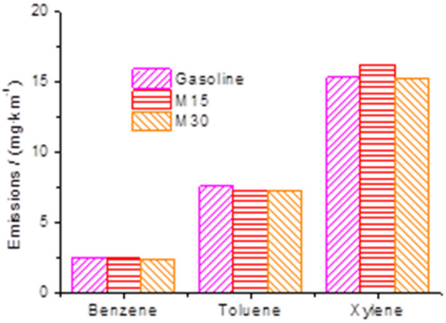
Average unregulated emissions at low temperature. Figure 5.33 shows the cycle average key unregulated emissions of gasoline, M15, and M30 three fuels at low temperature. Figure 5.34 shows the cycle average key unregulated emissions of gasoline, E10, and E20 three fuels at low temperature.

Seen from Figure 5.33(a), as the increase of the methanol proportion in fuels, methanol and formaldehyde emissions increase significantly at low temperature, while acetaldehyde emissions increase slightly. The methanol emission of M30 is 41.6 times as high as that of gasoline, while M15 is 15.7 times higher as that of gasoline. Besides, formaldehyde emissions of M30 and M15 are respectively 5.1 times and 2.4 times as high as that of gasoline. Acetaldehyde emissions of M30 and M15 fuels are respectively 132% and 110% of that of gasoline. Acetone emission decreases with the increase of methanol content in fuels, while the variation is slight. Acetone emissions of M30 and M15 are 90% and 93% of that of gasoline. Figure 5.33(b) shows benzene, toluene, and xylene emissions decrease with the increase of methanol content in fuels. Benzene emission of M30 is 75% of that of gasoline, while M15 is 80% of that of gasoline. The toluene emissions of M30 and M15 are 90% and 92% of that of gasoline. The xylene emissions of M30 and M15 are 59% and 89% of that of gasoline. Seen from Figure 5.33(c), the 1,3-butadiene emission at low temperature decrease with the increasing methanol proportion in the fuel, while the ethylene, propylene, and isobutene emissions remain basically the same. The 1,3-butadiene emissions of M30 and M15 are respectively 51% and 86% of that of gasoline. The results indicate that unburned methanol and formaldehyde emissions increase significantly. Using M30 fuel during the rapid acceleration condition at low temperature has been beyond the normal calibration range of general gasoline engine. Fuels which have methanol content higher than 30% cannot be directly used in gasoline engine.

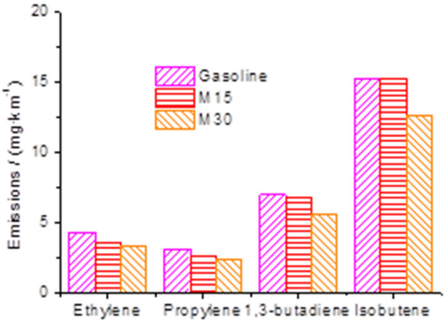
During the aldehydes and ketones emission shown in Figure 5.34(a), acetaldehyde emissions increase proportionally with the increase of the ethanol content in fuels at low temperature. Acetaldehyde emissions of E20 and E10 fuels are 3.2 times and 2.4 times as high as that of gasoline, while has a similar characteristic as normal temperature. Formaldehyde emission is nearly independent of the effects of the ethanol proportions in fuels, while acetone emission decreases slightly with the increase of the ethanol content in fuels. Figure 5.34(b) shows that benzene and xylene emissions decrease proportionally with the increase of the ethanol proportion in fuels. Toluene emissions of gasoline, E10, and E20 three fuels remain nearly unchanged. The benzene emission of E20 is 69% of that of gasoline, while E10 is 77% of gasoline. The xylene emissions of E20 and E10 are about 94% and 90% of that of gasoline. Seen from Figure 5.34(c), ethylene, propylene, and 1,3-butadiene emissions decrease significantly with the increase of the ethanol content in fuels at low temperature, while isobutylene emission keeps stable. The ethylene emission of E20 is 66% of that of gasoline, while E10 is 82% of gasoline. The propylene emissions of E20 and E10 are about 70% and 68% of that of gasoline, while the 1,3-butadiene emissions of E20 and E10 are 38% and 43% of that of gasoline.



(a) Alcohols, aldehydes and ketones

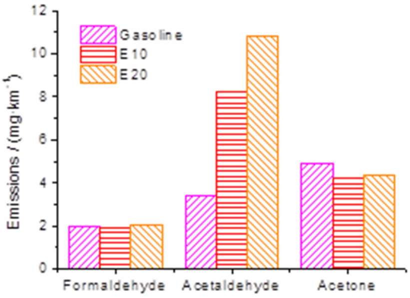


(b) Aromatic hydrocarbons

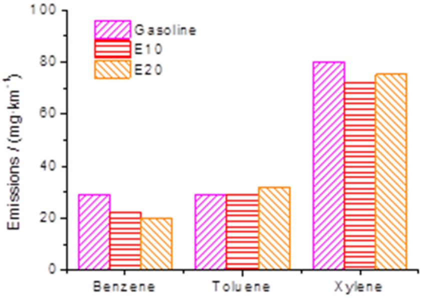


(c) Olefins

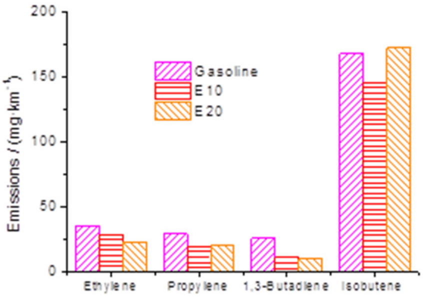
Figure 5.33 Effects of methanol proportions in fuels on cycle average unregulated emissions at low temperature



(a) Aldehydes and ketones



(b) Aromatic hydrocarbons



(c) Olefins

Figure 5.34 Effects of ethanol proportions in fuels on cycle average unregulated emissions at low temperature

Generally speaking, the characteristics of various unregulated emissions varying with the alcohols content in fuels at low temperature are similar as those at normal temperature. However, the change of various emissions at low temperature has a tendency to enlarge compared with that at normal temperature, especially for methanol, formaldehyde, 1,3-butadiene emissions of methanol-gasoline fuels and acetaldehyde emissions of ethanol-gasoline fuels.

Table 5.2 gives the comparison results of various unregulated emissions at low temperature and at normal temperature. The test results indicate that various unregulated emissions increase significantly at low temperature, similar with regulated emissions.

For low proportion of methanol gasoline fuels, the increase value of methanol emissions is the largest. The ratios of methanol emissions at low temperature to those at normal temperature of gasoline, M15, M30 three fuels are 4.5, 32.0, and 45.3. However, the increase value of formaldehyde emissions decreases significantly. The ratios of formaldehyde emissions at low temperature to those at normal temperature are respectively 1.3, 2.8, and 5.1. Benzene, ethylene, propylene and isobutylene emissions at low temperature are about 10~15 times as high as those at normal temperature, while low-temperature acetaldehyde, acetone, toluene, xylene, 1, 3-butadiene emissions are 2 ~ 6 times higher as those at normal temperature.

Table 5.2 Comparison of unregulated emissions at low temperature and normal temperature

Pollutants	Ratios of methanol fuels			Ratios of ethanol fuels		
	Gasoline	M15	M30	Gasoline	E10	E20
Methanol	4.5	32.0	45.3	——	——	——
Formaldehyde	1.3	2.8	5.1	1.1	1.1	1.1
Acetaldehyde	3.0	3.6	4.9	3.1	5.3	5.8
Acetone	2.3	1.9	1.8	4.0	3.5	3.9
Benzene	11.2	9.4	9.1	13.9	11.6	11.8
Toluene	3.8	3.6	3.6	6.6	6.9	8.0
Dimethylbenzene	5.9	4.9	3.4	14.3	13.6	14.5
Ethylene	9.2	11.5	11.8	8.9	7.8	7.1
Propylene	11.2	14.6	14.9	8.5	6.6	7.4
1,3-Butadiene	4.1	3.6	2.6	4.4	2.1	2.2
Isobutene	11.0	11.7	12.7	18.5	17.1	23.0

For low proportion of ethanol gasoline fuels, the ratios of acetaldehyde emissions at low temperature to those at normal temperature of gasoline, E10, E20 three fuels are respectively 3.1, 5.3 and 5.8. The ratios of formaldehyde emissions at low temperature to those at normal temperature of three fuels are almost 1.1. Benzene, xylene and isobutylene emissions at low temperature are 10 times higher than those at normal temperature. Low-temperature acetone and 1,3-butadiene emissions are about 2~5 times as high as those at normal temperature, while toluene, ethylene, and propylene emissions at low temperature are about 6~9 times higher as those at normal temperature.

Comprehensively speaking, with the increase of the alcohol proportions in fuels, the ratios of methanol, formaldehyde, acetaldehyde emissions at low temperature to those at normal temperature have a tendency to increase, while the ratios of benzene and 1,3-butadience fell slightly.

5.3.3 Evaporative emissions of alcohol fueled vehicles

Evaporative emissions of the same vehicle fuelled with gasoline, M15 and E10 fuels were measured according the Euro V standard. Formal evaporative emissions test contains two parts, which are hot soak and diurnal breathing process. The sum of HC mass during the two parts of hot soak and diurnal breathing process is the total result of the evaporative emissions test.

The light-duty vehicle used VT-6500-P-HO sealed chamber is a temperature variable and volume changeable room, which is utilized to measure the evaporative emissions and refueling emissions of light-duty vehicles. The HC measurement system is MEXA-1170 type heated flame ionization detector. The measuring range is 0~20000ppmc. The sampling rate is 2L/min. The measurement accuracy is ±1%. The response time T90 is 1.5s.

The aromatic hydrocarbon pollutants emissions in the sealed chamber at the end of diurnal breathing process were collected by TENAX absorption tubes and analyzed by GC-MS. In the mean while aldehydes and ketones pollutants emissions during the diurnal breathing process were sampled by DNPH adsorption column and analyzed by HPLC.

Regulated pollutants evaporative emissions. Figure 5.35 shows HC evaporative emissions during the hot soak, diurnal breathing, and the whole process of the same vehicle using E10, gasoline and M15 three fuels. Seen from the figure, HC emissions of E10 and M15 fuels are respectively 130% and 125% of that of gasoline during the hot soak process. It indicates that the alcohols content in fuels belong to low carbon compounds, which could be more easily exhausted from the fuel supply system as the vehicle is in the hot condition. HC emissions of E10 and gasoline fuels during the diurnal breathing process are basically the same, while the HC emissions of M15 fuel is about 108% of that of gasoline. Totally speaking, HC emissions of E10, gasoline, M15 three fuels during the whole process of evaporative test are similar. The total HC emissions of E10 and M15 fuels are respectively 102% and 110% of that of gasoline, which indicates the additive of low proportional alcohols into fuels does not have worse effects on the evaporative emissions of light-duty vehicles. Figure 5.36 gives the HC transient evaporative emission curve of different fuels during the diurnal breathing process. The figure shows HC transient evaporative emission curve of E10 fuel is almost the same as that of gasoline. However, M15 fuel has the trend of increasing slowly first and fast afterwards. More HC evaporative emission can be produced in the later stage of diurnal breathing process.

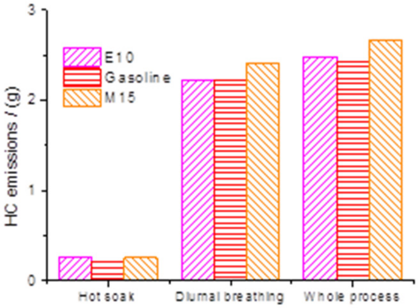


Figure 5.35 HC Evaporative emissions of different fuels

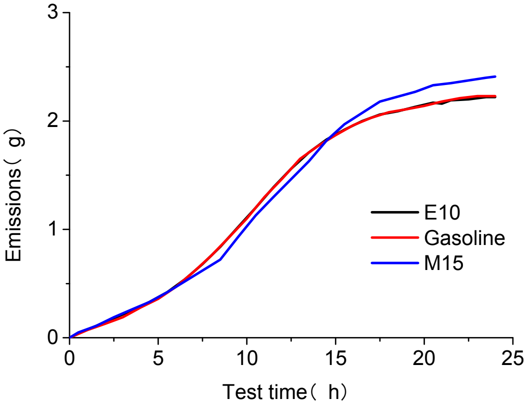
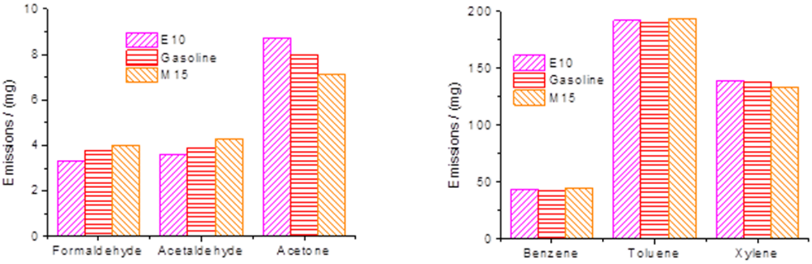


Figure 5.36 HC instantaneous evaporative emissions of different fuels during the diurnal breathing process

Unregulated pollutants evaporative emissions. Figure 5.37 shows the unregulated pollutants evaporative emissions of different fuels during the diurnal breathing process. Seen from the figure, there are some differences among various unregulated pollutants evaporative emissions of three fuels during the diurnal breathing process, though the variation is small. The evaporative emissions of formaldehyde and acetaldehyde are about 4mg, while that of acetone is about 8mg. The evaporative emissions of aromatic hydrocarbons are bigger, while evaporative emissions of benzene, toluene, and xylene are about 40 mg, 190 mg, and 130 mg. The test results indicate that the additive of alcohols into gasoline will not produce more evaporative emissions of aldehyde, ketones and aromatic hydrocarbons pollutants.

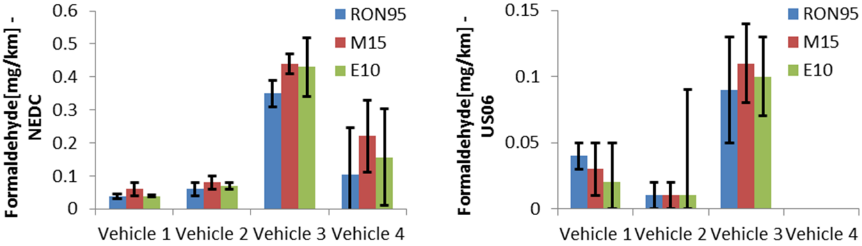


(a) Aldehydes and ketones (b) Aromatic hydrocarbons

Figure 5.37 Unregulated evaporative emissions of different fuels during the diurnal breathing process

5.4 Israel

Figure 5.38 shows the plots of Carbonyl Emissions during NEDC and US06. Each data point represents the average of at least three independent measurements as described in the relevant section.



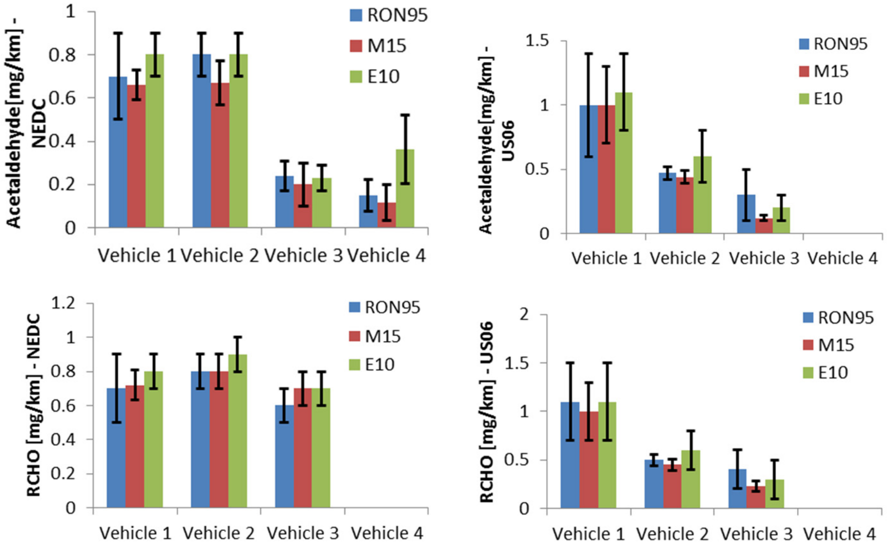


Figure 5.38 Plots of Carbonyl Emissions (NEDC and US06)

In addition, Welch's test was used in order determine whether there is a statistical significance (for 90% confidence) between the base fuel (RON95) and the other tested fuels (M15 & E10) regarding each measured emission.

$$t = \frac{\overline{X1} - \overline{X2}}{\sqrt{((\sigma_1^2/N_1) + (\sigma_2^2/N_2)\ )}}$$

The data points that have 90% statistical significance in relation to the base fuel (RON95) are bolded and underlined in the tabulated results.

The error bars in the data plots present the standard deviation. Results that have 90% confidence are marked with an asterisk.

The US06 is a hot start cycle, while the NEDC is a cold start cycle. Overall for the NEDC driving cycle, a large portion of the emissions were emitted during the first phase of the cycle (UDC), since during this phase, the engine and the catalectic converter are far from their working temperature. The combined effect of a fuel-rich mixture that will support ignition during the cold start and the low temperature of the catalytic converter, which is lower than its light-up temperature, increases the emissions per km substantially in comparison to the EUDC phase.

Formaldehyde

- Of the seven results for all the cycles (three for US06 and four for NEDC), five show that the amount of emitted formaldehyde when using M15 is slightly higher than it is when using RON95. Two results show that formaldehyde emission for M15 is lower than for RON95.
- Of these results, one showed statistical significance with confidence of 90%.
- All the measurements were considerably below the California legal limit of 4mg/mile.

Acetaldehyde

- All seven results for the cycles (three for US06 and four for NEDC) show that when using M15 the amount of emitted acetaldehyde is lower than it is when using RON95.
- None of the results shows statistical significance with confidence of 90%.

RCHO

- Of the six results for all the cycles (three each for US06 and NEDC), four show that the amount of emitted carbonyls is lower when using M15 than it is when using RON95. Two results show that carbonyls for M15 are lower than for RON95.

- None of the results shows statistical significance with confidence of 90%.

Chapter 6 Comparison Results of Different Test Cycles

This chapter mainly introduces the comparison emissions tests of the same light-duty vehicle fuelled with E10 fuel during European, American and Japanese emissions regulations on a chassis dynamometer, and researches the influences of different driving cycles on the regulated and unregulated emissions.

Using a light-duty vehicle fuelled with the same fuel, emission tests during European, American and Japanese emissions regulations were carried on a chassis dynamometer. FTIR, HPLC and GC-MS methods were utilized to measure methanol, formaldehyde, acetaldehyde, acetone, benzene, toluene, xylene, ethylene, propylene, 1,3-butadiene and isobutylene unregulated emissions in the vehicle exhaust. Due to the differences of actual driving conditions in each country, the detailed test parameters of above-mentioned test cycles are consequently different. The total mileage and total time of the American FTP75 cycle is the longest. The cycle phases are diverse, containing cold start stage, transition stage and hot start stage. The European NEDC cycle consists of two test stages. The cycle parameter is located in the middle of the three test cycles, combining the driving conditions in urban area and suburb. Due to the small size of national territorial area, Japan JC08 cycle mainly indicates the driving conditions of vehicles in the crowded city. Therefore, the cycle mileage is short and the test time is long. The average speed and the maximum speed of Japan cycle are lower than that of European and American cycles.

6.1 Instantaneous regulated emissions results

Figure 6.1~6.3 respectively gives the instantaneous emissions curves of CO, HC and NO_X regulated pollutants during JC08, FTP75 (the first and second stage), and NEDC cycles using the same light-duty vehicle.

Seen from Figure 6.1, in Japan JC08 driving cycles, the first peak of CO emission occurred in 15s after the cold start and was about 100×10^{-6}. During the curves, the highest instantaneous peak of CO emissions occurred in the first rapid accelerating condition (about 40s) and reached 300×10^{-6}. Subsequently there was a small peak occurring in the each rapid accelerating condition. The first peak of HC emissions also occurred in 15s after the cold start and remained till 50s, which was about 200×10^{-6}. The emissions gradually reduced to nearly zero and then maintained zero-emission level until the end of the JC08 cycle. The maximum peak of NO_X emission (about 80×10^{-6}) occurred in the first rapid acceleration condition (about 40s), then gradually reduced to zero and maintained, similar with HC emission.

As shown in Figure 6.2, during the American FTP cycle, CO emission had the first and the maximum peak in 15s after the cold start, which was about 120×10^{-6}. Subsequently there were a few peaks not more than 100×10^{-6} occurring in the rapid acceleration conditions. HC emission had two peaks occurring in the first rapid acceleration condition (about 35s) and the maximum acceleration condition, which were respectively 300×10^{-6} and 50×10^{-6}. Similar with HC emission, two peaks of 270×10^{-6} and 80×10^{-6} occurred in the 35s and 200s, which were higher than those NO_X emissions shown in Figure 6.1.

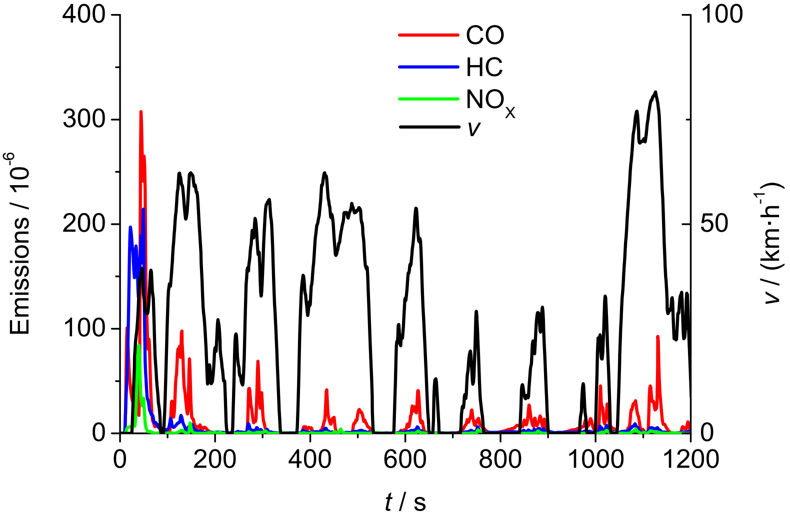


Figure 6.1 Instantaneous regulated emissions during Japan JC08 cycle

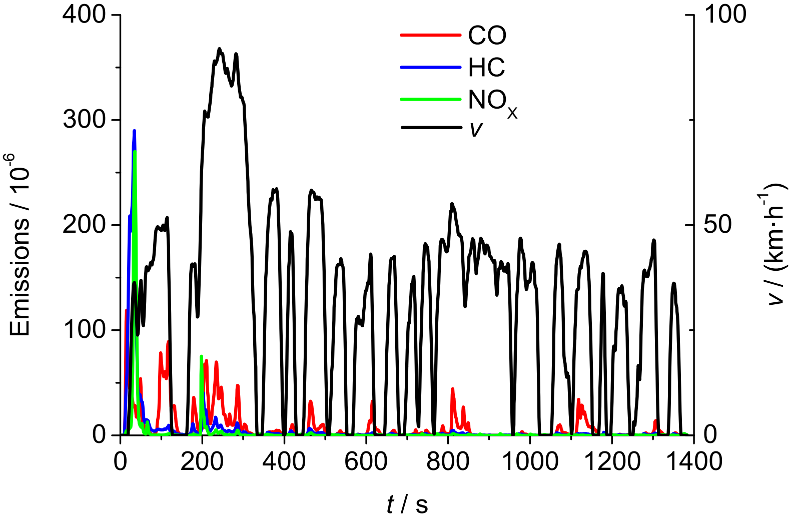


Figure 6.2 Instantaneous regulated emissions during USA FTP75 cycle

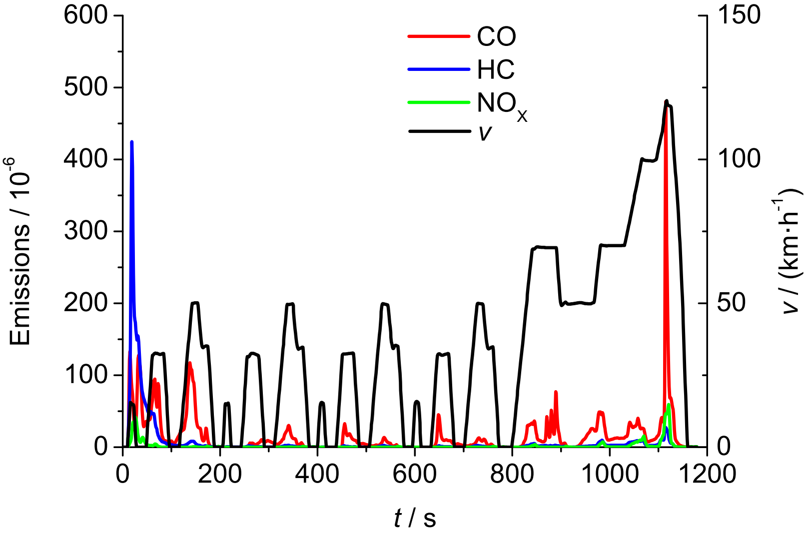


Figure 6.3 Instantaneous regulated emissions during Euro NEDC cycle

Seen from Figure 6.3, during the European NEDC cycle, CO emissions had a peak not more than 150×10^{-6} occurring in every rapid acceleration conditions. The maximum peak occurred in the last acceleration conditions with the highest speed (about 1115s), which was 480×10^{-6}. The peak of HC emission occurred in the first rapid acceleration conditions (about 20s), which was about 420×10^{-6}. And then it gradually reduced to nearly zero level. NO$_X$ emission had two peaks in 20s and 1115s, which were 40×10^{-6} and 60×10^{-6}.

6.2 Instantaneous unregulated emissions results

Figure 6.4~6.7 respectively gives the instantaneous emissions curves of methanol, formaldehyde, benzene, and 1,3-butadiene unregulated pollutants during JC08, FTP75 (the first and second stage), and NEDC cycles using the same light-duty vehicle. Seen from the three figures, the instantaneous unregulated pollutants emissions curves of JC08, FTP75, and NEDC three cycles had the similar characteristics. The methanol, formaldehyde, benzene and 1,3-butadiene emissions had the first and largest peak in 25s after the cold start. However the peak values of the three cycles were slightly different. Subsequently various unregulated pollutants emissions quickly reduced to nearly zero level and remained till the end of driving cycles. Hereinto, the peak values of methanol, formaldehyde, benzene, and 1,3-butadiene emissions during the Japan JC08 cycle were the largest, which were respectively 25×10^{-6}, 20×10^{-6}, 40×10^{-6}, and 110×10^{-6}.

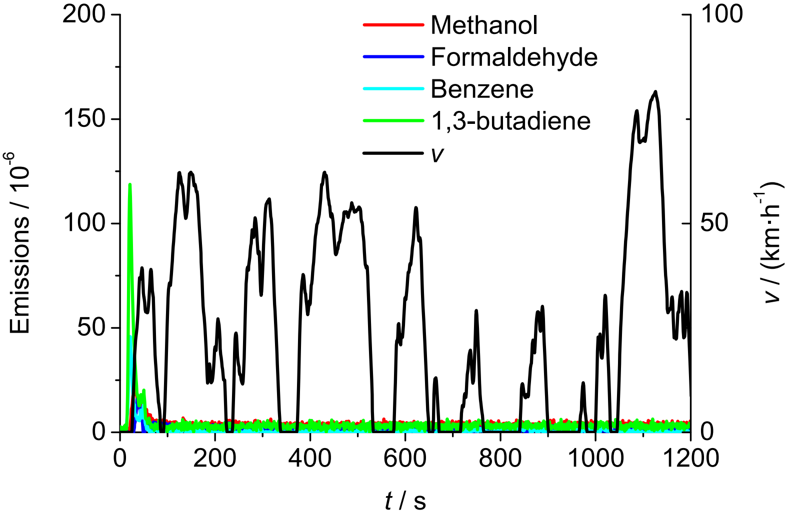


Figure 6.4 Instantaneous unregulated emissions during Japan JC08 cycle

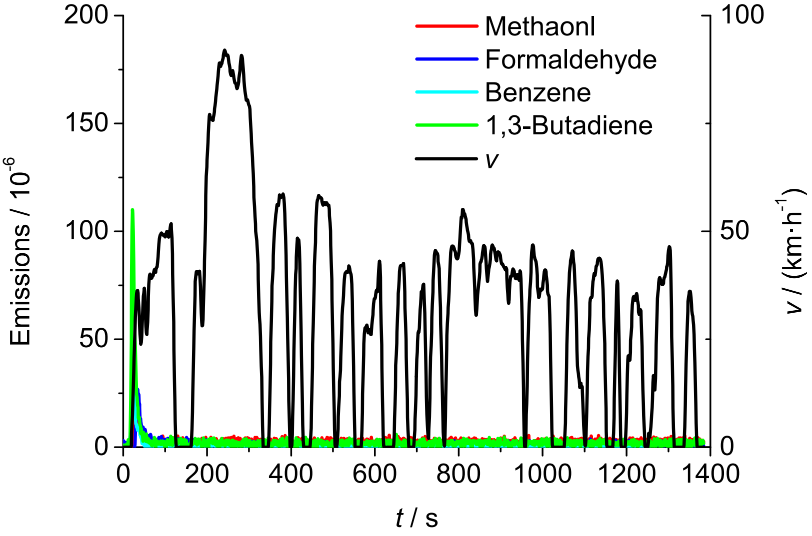


Figure 6.5 Instantaneous unregulated emissions during USA FTP75 cycle

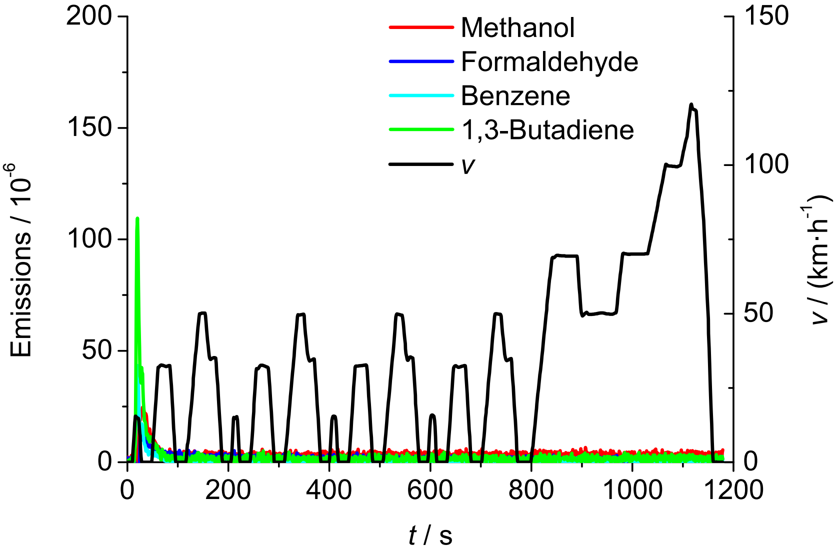


Figure 6.6 Instantaneous unregulated emissions during Euro NEDC cycle

6.3 Cycle average emissions results

According to the above-mentioned instantaneous pollutants emissions curves, the average emissions levels of different driving cycles were calculated. Figure 6.7 and 6.8 shows respectively the average emissions levels of CO, HC, NO_X, CO_2, CH_4 regulated pollutants and methanol, formaldehyde, acetaldehyde, acetone, benzene, toluene, dimethylbenzene, ethylene, propylene, 1,3-butadiene, isobutene unregulated pollutants.

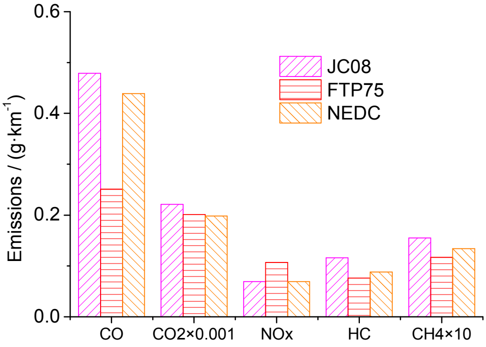
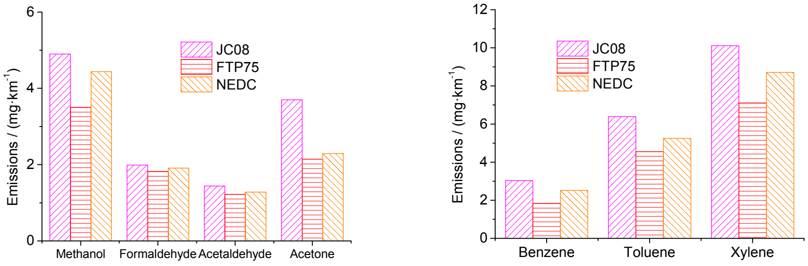
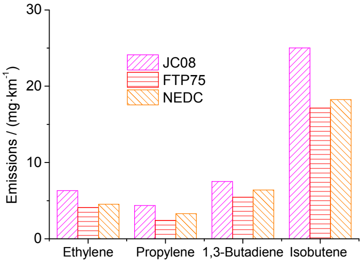


Figure 6.7 Cycle average regulated emissions of different cycles

The test results indicate that, although there are differences in the average emission levels during different driving cycles, the largest variation is not more than 2 times. Seen from Figure 6.7, the average levels of CO, HC, CO_2 and CH_4 emissions using the same light-duty vehicle have the same tendency: Japanese JC08> European NEDC> American FTP75, while NO_X emissions have the opposite tendency: American FTP75> European NEDC> Japanese JC08. Figure 6.8 shows that the average emissions levels of alcohols, aldehydes, ketones, aromatic hydrocarbons, and olefins unregulated pollutants have the same tendency as HC and CO emissions: Japanese JC08> European NEDC > American FTP75.



(a) Alcohols, aldehydes and ketones (b) Aromatic hydrocarbons



(c) Olefins

Figure 6.8 Cycle average unregulated emissions of different cycles

Seen from the comparison of instantaneous emissions curves, there was a rapid acceleration conditions at the cold start during the American FTP75 cycle, while the engine and catalyst did not reach a steady state. A high peak of NO_X emission occurred in the vehicle exhaust, causing the average emission level of NO_X during the American FTP75 cycle was the highest. CH_4, methanol, formaldehyde, acetaldehyde, acetone, benzene, toluene, xylene, ethylene, propylene, and 1,3-butadiene pollutants are all hydrocarbons. In case that the light-duty gasoline vehicle does not change the fuel, the characteristics of these pollutants vary with driving cycle conditions should be consistent with HC emission.

Chapter 7 Conclusions and Summary

With the reduction of regulations restricting emissions and the application of alternative fuels, unregulated emissions in automobile exhaust have gradually attracted the attention. The hazards of polycyclic aromatic hydrocarbons, aldehydes, ketones, and olefins on the environment and human health cannot be ignored. However, the key issues of measurement methods and quantitative analysis on unregulated emissions need to conduct in-depth research at this stage.

7.1 Finland results

The effect of test temperature was evident for the most emissions. CO and HC emissions were higher at -7°C than at +23°C in the cold start NEDC test, particularly with the MPI car. E85 reduced the CO emission, but increased HC emissions when compared with E10. The dominating hydrocarbons present were methane, ethene, xylenes and acetylene for E85, whereas aromatics, methane and ethene dominated for E10. Ethanol emission was huge for the E85 fuel at -7°C. Formaldehyde and acetaldehyde emissions were higher for the E85 fuel than for the E10 fuel in the cold-start NEDC test. Acetaldehyde was formed in substantial concentrations in 3 minutes after the cold-start of car, whereas emission level was low with warmed-up engine.

The NO_X emissions were relatively low over the NEDC test and only small differences between fuels were detected. Surprisingly high NO_X emissions were observed over the hot start FTP75 test, particularly after a 10 minutes pause. This indicates that cars may be optimised towards low CO and HC emissions at a cost of increased NO_X

emissions. Nitrogen dioxide and nitrous oxide emissions were mostly below the detection limit of measurement equipment. In the opposite, ammonia emissions were substantial. Ammonia concentrations continuously exceeded 10 ppm, which is a limit value for SCR equipped heavy-duty engines, and even as high as 300-500 ppm concentrations were observed. Ammonia is formed by the three-way catalysts of the spark-ignited cars, and by the use of urea-based SCR systems for NO_X control for diesel vehicles.

PM emissions were low: below 7 mg/km in the NEDC test and below 1 mg/km in the hot-start FTP75 test. However, a slight decrease in PM emission was observed with increasing ethanol content of fuel. “Wet” particle number emissions (PN) were higher at -7°C than at +23°C in the NEDC test and higher for E10 than for E85. Nucleation tendency was seen for the MPI car, whereas accumulation mode particles dominated for the DISI car.

E100 was tested only at +23 °C temperature, because the startability limit of neat ethanol is only around +12 °C. Both cars experienced serious starting and driveability problems in the beginning of test with E100, whereas no problems occurred with warmed-up engine. The overall emissions were higher for E100 than for E85, though particle mass and number emissions were low.

E85 fuel typically reduces CO, HC, and NO_X emissions compared with gasoline at normal temperature, but not necessarily at low temperatures. Excess fuel is injected in cold starts due to the poor ignition of ethanol, which tend to increase for example acetaldehyde emission before the engine is warmed-up at cold temperatures. Engine and emissions control technology of FFV cars are developing to overcome elevated cold-start emissions when using the E85 fuel, but the FFV cars in this study still showed a strong temperature-dependence. High emissions occurred only for the first kilometers after a cold-start, however, driving distances for gasoline cars are generally short in real-life. In sub-zero temperatures, block heaters could efficiently reduce cold-start emissions.

7.2 Canada results

In general it was found that changes in the emission rates of pollutants and in fuel consumption due to the use of E10 was dependent on the drive cycle, test conditions and vehicle technology. The use of E85 led to reduced TPM, particle number, and tailpipe CO_2 equivalent greenhouse gas emission rates; however these reductions came with roughly a 30% increase in fuel consumption and substantial increases in acetaldehyde emissions. The use of E85 lowered the GDI TPM emission rate to a range similar to that of the PFI.

The emission rates of formaldehyde and acetaldehyde were 3 and 9 times higher respectively with the use of E85 compared to E0 and tested at 22°C. The increases in emissions of these compounds were more pronounced at cold temperature, for example acetaldehyde was roughly two orders of magnitude higher on E85 than on E0 at -18°C.

BTEX emission rates were approximately 70% to 84% lower with use of the E85 fuel compared to E0 at 22°C. Reductions in BTEX by approximately 50% were also observed at -7°C and, to a lesser extent at-18°C, due to the use of the E85 fuel; however, for the most part, these reductions were not statistically significant at -18°C due to sample variability.

The use of E85 also decreased the particle number emission rate by 78% to 90% compared to E0. There was also a shift to a lower primary peak diameter, from 70-80nm to as low as 34nm at 22°C, due to the use of E85.

The GDI had better fuel economy and used 14-30% less fuel than the PFI over the three test cycles. The GDI had higher TPM emission rates at 22°C but this trend was reversed at cold temperature where the emission rate of the PFI exceeded that of the GDI. Interestingly the particle number emission rate of the PFI remained lower than that of the GDI regardless of the test cell temperature indicating that the particles emitted by the PFI at cold temperature contributed more mass than those of the GDI due possibly to a shift to larger particle sizes.

As expected, decreasing the ambient test temperature led to increases in the emission rates of almost all measured pollutants.

7.3 China results

Using a light-duty gasoline vehicle fuelled with the same fuel, emission tests during European, American and Japanese emissions regulations were carried on a chassis dynamometer. Using two PFI vehicles and two GDI vehicles fuelled with pure gasoline, M15, M30 and pure gasoline, E10, E20 separately, 25℃ normal temperature emission test, -7℃ low temperature emission test and evaporation emission test were carried on.

Comparing the transient emissions and average emissions during the driving cycle of major pollutants, the good consistency of MEXA, FTIR, HPLC and GC-MS measurement methods has been verified. The deviations of the average regulated and unregulated emissions measured by various measurement methods are basically in the range of ± 10%.

From the light-duty gasoline vehicle using alcohols fuels, the transient emissions of formaldehyde, acetaldehyde, toluene, propylene and 1,3-butadiene have the highest peak during the first acceleration condition. Then with the catalyst lights off, the emissions values gradually reduce to nearly zero and remain until the end of the driving cycle. In the low as well as normal ambient temperature, as the alcohols proportion increasing in the fuel, CO_2 in the exhaust emissions remain basically the same, HC, CO and CH_4 decrease slightly, NO_X increases slightly, unburned methanol, formaldehyde, acetaldehyde increase proportionally, benzene, toluene, ethylene, propylene, 1,3-butadiene and isobutene decrease slightly. The regulated and unregulated emissions in the low ambient temperature are significantly higher than those in the normal ambient temperature. The average unregulated emissions levels of GDI and PFI test vehicles are in the same order of magnitude. The regulated and unregulated emissions have the good consistency. The difference of HC emissions in the entire process of the evaporative emission tests of E10, gasoline and M15 fuels is slight. Although there is a difference of unregulated emissions in the diurnal test of three fuels, the difference is very small.

Although there are differences in the average emission levels from the same light-duty vehicle during different driving cycles, the largest variation is not more than 2 times. Opposite with NO_X emissions, the average levels of CO, HC, CO_2, CH_4, aromatic hydrocarbons, aldehydes, ketones, and olefins emissions have the same tendency: Japanese JC08> European NEDC> American FTP75.

7.4 Israel results

Oxygenated fuels tested at this research did not change the amount of emitted formaldehyde compared to RON95. Oxygenated fuels tested at this research may decrease the amount of emitted acetaldehyde compared to RON95. Oxygenated fuels tested at this research did not change the amount of emitted carbonyls compared to RON95. It is concluded that using M15 does not have statistically significant effects on carbonyl emissions.

References

[1] Shangxi Province ”National Methanol Vechile Demonstration Project” Project Group. Feasibility Report on Promotion of China’s methanol fuel and vehicle[J]. 2005

[2] Charalampos I A, Anastaslos N K, Panagiotis D S. Behavior of a Small Four-Stroke Engine Using as Fuel Methanol-Gasoline Mixtures. SAE Paper 2003-32-0024

[3] Hasan M A. Effect of ethanol-unleaded gasoline blends on engine performance and exhaust emission. Energy Conversion and Management, 2003, 44(9): 1547-1561

[4] Vaughan R B, William J K, Jack D B, et al. Emissions with Reformulated Gasoline and Methanol Blends in 1992 and 1993 Model Year Vehicles. SAE Paper 1994: 941969

[5] Knapp K T, Stump F D, Tejada S B. Effect of ethanol fuel on the emissions of vehicles over a wide range of temperatures. J Air & Waste Management Association, 1998, 48 (7): 646-653

[6] Poulopoulos S G, Samaras D P, Philoppopoulos C J. Regulated and unregulated emissions from an internal combustion engine operating on ethanol containing fuels. Atmospheric Environment, 2001, 35(26): 4399-4406

[7] Yan X, Huang H, Huang X. Evaluation of toxicity and environmental impact of vehicle-used methanol fuel. J Occu Heal Dam, 2004; 19(2): 117-118.

[8] Rutten G A, Burtner C W J, Visser H, et al. The Determination of aldehydes in the exhaust gases of LPG fulled engines. Chromatographia, 1998(26): 274-280

[9] Sergio M C, Graciela A. Carbonyl emissions in diesel and biodiesel exhaust. Atmospheric Environment, 2007, 41: 5436-5441

[10] Wei Yanju, Liu Shenghua, Li Hongsong, et al. Effects of Methanol/Gasoline Blends on a Spark Ignition Engine Performance and Emissions. Energy & Fuels, 2008(22): 1254-1259

[11] Liu Shenghua, Eddy R. Cuty Clemente, Hu Tiegang, et al. Study of spark igntion engine fueled with methanol/gasoline fuel blends. Applied Thermal Engineering, 2007(27): 1904-1910

[12] Wei Yanju, Liu Shenghua, Liu Fangjie, et al. Formaldehyde and Methanol Emissions from a Methanol/Gasoline-Fueled Spark-Ignition (SI) Engine. Energy & Fuels, 2009(23): 3313-3318

[13] Charlotte S, Lennart E, Jan G, et al. Measurement Methodologies for Hydrocarbons, Ethanol and Aldehyde Emissions from Ethanol Fuelled Vehicles. SAE Paper 2010-01-1557.

[14] Zhang, Z., Fang, G., Song, C. et al., "Unregulated Emissions Characteristics from SI Electronic Control Methanol Engine," Journal of Combustion Science and Technology, 2006, 12(1): 86-89, doi:CNKI:SUN:RSKX. 0.2006-01-018.

[15] Zhang, H., Li, J., Wang, L. et al., "Measurement of formaldehyde emission from an engine fuelled by gasoline-methanol blends," Journal of Jilin University (Engineering and Technology Edition), 2008, 38(1):32-36, doi: CNKI:SUN:JLGY.0.2008-01-007.

[16] Kelly, K., Bailey, B., Coburn, T., Clark, W. et al., "FTP Emissions Test Results from Flexible-Fuel Methanol Dodge Spirits and Ford Econoline Vans," SAE Technical Paper 961090, 1996, doi:10.4271/961090.

[17] Ge, Y., You, K., Wang, J. et al., "A Study on Exhaust Emission from Methanol Vehicle," Transactions of Beijing Institute of Technology, 2008, 28(4):314-318, doi: CNKI:SUN:BJLG.0.2008-04-010.

[18] Zhang, F., Zhang, X., Shuai, S. et al., "Unregulated Emissions and Combustion Characteristics of Low-Content Methanol−Gasoline Blended Fuels," Energy Fuels, 2010, 24 (2):1283–1292, doi:10.1021/ef900974p.

[19] Liu, F., Wei, Y., Liu, S. et al., "Unregulated Emissions and Their Three-Way Catalytic Conversion of a Spark Ignition Engine Fueled with Ethanol-Gasoline," Journal of Xi'an Jiaotong University, 2010, 44(1):13-16, doi: CNKI:SUN:XAJT.0.2010-01-005.

[20] He, B., Wang, J., Hao, J. et al., "A study on emission characteristics of an EFI engine with ethanol blended gasoline fuels," Atmospheric Environment, 2003, 37(7):949-957, doi:10.1016/S1352-2310(02)00973-1.

[21] Dong, S., Song, C., Zhao, C. et al., "Unregulated Emissions from Gasoline Engine Using Ethanol-Blended Gasoline as Fuels," Journal of Tianjin University, 2006, 39(1):68-72, doi:CNKI:SUN:TJDX.0.2006-01-016.

[22] Aakko, P. and Nylund, N.-O. (2003) Particle emissions at moderate and cold temperatures using different fuels. Warrendale: Society of Automotive Engineers. SAE Paper 2003-01-3285.

[23] Aakko-Saksa, P., Rantanen-Kolehmainen, L., Koponen, P., Engman, A. and Kihlman, J. (2011) Biogasoline options – Possibilities for achieving high bio-share and compatibility with conventional cars.

SAE International Journal of Fuels and Lubricants, 4:298–317 (also SAE Technical Paper 2011 24-0111). Full technical report: http://www.vtt.fi/inf/pdf/workingpapers/2011/W187.pdf

[24] Alhajeri, N.S., McDonald-Buller, E.C., Allen, D.T. (2012) Impacts of replacement of gasoline and diesel with biofuels on ozone concentrations: a central Texas case study. Air and Waste Management Association Annual Conference and Exhibition, 105th, San Antonio, TX, United States, June 19-22, 2012 (2012), 2, 1323-1327.

[25] Chiba, F., Ichinose, H., Morita, K., Yoshioka, M., Noguchi, Y. and Tsugagoshi, T. High Concentration Ethanol Effect on SI Engine Emissions (2010) SAE Technical Paper 2010-01-1268.

[26] Clairotte, M., Adam, T. W., Zardini, A. A., Manfredi, U., Martini, G., Krasenbrink, A., Vicet, A., Tournie, E. and Astorga, C. (2013) Effects of low temperature on the cold start gaseous emissions from light duty vehicles fueled by ethanol-blended gasoline. Applied Energy (2013), 102, 44-54. DOI:10.1016/j.apenergy.2012.08.010.

[27] CRFA (2003) Canadian Renewable Fuels Association Website. http://www.greenfuels.org.

[28] De Serves, C. (2005) Emissions from Flexible Fuel Vehicles with different ethanol blends. AVL MTC AB, Sweden. Report No AVL MTC 5509. Online http://www.senternovem.nl/mmfiles/Emissions%20from%20flexible%20fuel%20vehicles_tcm24 280163.pdf.

[29] E85 Handbook (2010) Handbook for Handling, Storing, and Dispensing E85. US Department of Energy. DOE/GO-102010-3073.

[30] European Environment Agency (2012a) Air quality in Europe — 2012 report. EEA Report No 4/2012.

[31] European Environment Agency (2012b) The contribution of transport to air quality. EEA Report No 10/2012.

[32] Fridell, E., Haeger-Eugensson, M. Moldanova, J. Forsberg, B. and Sjoeberg, K. (2014) A modelling study of the impact on air quality and health due to the emissions from E85 and petrol fuelled cars in Sweden. Atmospheric Environment (2014), 82, 1-8. DOI:10.1016/j.atmosenv.2013.10.002

[33] Gaffney, J.S. and Marley, N.A. Beyond ozone and carbon dioxide: Ethene and its potential ecosystem impacts from biomass burning and ethanol biofuels. Abstracts, 67th Southwest Regional Meeting of the American Chemical Society, Austin, TX, United States, November 9-12 (2011), SWRM-231.

[34] Ginnebaugh, D.L. and Jacobson, M.Z. (2012) Examining the impacts of ethanol (E85) versus gasoline photochemical production of smog in a fog using near-explicit gas- and aqueous-chemistry mechanisms. Environmental Research Letters (2012), 7(4), 045901, 8 pp. DOI:10.1088/1748-9326/7/4/045901

[35] Graham, L., Belisle, S. and Baas, C.-L. (2008) Emissions from light duty gasoline vehicles oper-ating on low blend ethanol gasoline and E85. Atmospheric Environment 42(2008) 4498–4516.

[36] Haskew, H. and Liberty, T. (2006) Fuel permeation from automotive systems: E0, E6, E10, E20 and E85. Final report. CRC Project No. E-65-3.

[37] Hays, M.D., Preston, W., George, B.J., Schmid, J., Baldauf, R., Snow, R., Robinson, J.R., Long, T. and Faircloth, J. (2013) Carbonaceous Aerosols Emitted from Light-Duty Vehicles Operating on Gasoline and Ethanol Fuel Blends. Environmental Science & Technology (2013), 47(24), 14502-14509. DOI:10.1021/es403096v.

[38] Heeb N.V., Saxer C.J. et al. Correlation of hydrogen, ammonia and nitrogen monoxide (nitric oxide) emissions of gasoline-fueled Euro-3 passenger cars at transient driving. Atmospheric Environment, Vol 40, 2006, pp. 3750-3763.

[39] Huo, H., Wu, Y. and Wang, M. Total versus urban: Well-to-wheels assessment of criteria pollutant emissions from various vehicle/fuel systems. Atmospheric Environment (2009), 43(10), 1796-1804. DOI:10.1016/j.atmosenv.2008.12.025.

[40] IARC (1999). Re-evaluation of some organic chemicals, hydrazine and hydrogen peroxide. IARC Monogr Eval Carcinog Risks Hum, 71: 1–315. PMID:10507919

[41] IARC (2010). Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. IARC Monogr Eval Carcinog Risks Hum, 92: 1–853. PMID:21141735.

[42] IARC (2012). Arsenic, metals, fibres, and dusts. IARC Monogr Eval Carcinog Risks Hum, 100C: 1–499. PMID:23189751

[43] Jacobson, M. (2007) Effects of Ethanol (E85) versus Gasoline Vehicles on Cancer and Mortality in the United States. Environ. Sci. Technol. 2007, 41, 4150–4157.

[44] Karavalakis, G., Durbin, T., Shrivastava, M., Zheng, Z., Villela, M., Jung, H. (2012) Impacts of ethanol fuel level on emissions of regulated and unregulated pollutants from a fleet of gasoline light-duty vehicles. Fuel (2012), 93, 549-558. DOI:10.1016/j.fuel.2011.09.021.

[45] Karlsson, H., Gåste, J. and Åsman, P. (2008) Regulated and non-regulated emissions from Euro 4 alternative fuel vehicles. Society of Automotive Engineers. Warrendale. Tech-nical Paper 2008-01-1770.
[46] Kassel, R. (2006) An Environmental Perspective: EPA's RFS Proposal. Presentation in the meet-ing of Mobile Sources Technical Review Subcommittee (MSTRS), October 4, 2006.
[47] Laurikko, J., Nylund, N-O., Aakko-Saksa, P. (2013) High-volume ethanol fuel composition optimized for cold driving conditions. Warrendale: Society of Automotive Engineers. SAE Technical Papers 2013-01-2613. doi-link: 10.4271/2013-01-2613.
[48] Li, W., Perry, K., Narayanaswamy, K., Kim, C. et al., (2010) Passive Ammonia SCR System for Lean-burn SIDI Engines, SAE Int. J. Fuels Lubr. 3(1):99-106, 2010, doi:10.4271/2010-01-0366.
[49] Mejia-Centeno, I., Martínez-Hernández, A. and Fuentes, G. (2007) Effect of low-sulfur fuels upon NH3 and N2O emission during operation of commercial three-way catalytic converters. Topics in Catalysis. Vols. 42–43, May 2007.
[50] Millet, D.B., Apel, E., Henze, D., Hill, J., Marshall, J.D., Singh, H.B. and Tessum, C.W. (2012) Natural and Anthropogenic Ethanol Sources in North America and Potential Atmospheric Impacts of Ethanol Fuel Use. Environmental Science & Technology (2012), 46(15), 8484-8492. DOI:10.1021/es300162u.
[51] Nopmongcol, U., Griffin, W.M., Yarwood, G., Dunker, A.M., MacLean, H.L., Mansell, G. and Grant, J. (2011) Impact of dedicated E85 vehicle use on ozone and particulate matter in the US. Atmospheric Environment (2011), 45(39), 7330-7340. DOI:10.1016/j.atmosenv.2011.07.057.
[52] The Nordic Ecolabelling (2008) Swan labeling of fuels. Version 1.0. 25 June 2008 – 30 June 2010.
[53] OEHHA (2009) Technical support document for cancer potency factors. California Environmental Protection Agency. Office of Environmental Health Hazard Assessment. May 2009.
[54] Querini F, Béziat JC, Morel S, Boch V, Rousseaux P (2011) Life cycle assessment of automotive fuels: critical analysis and recommendations on the emissions inventory in the tank to wheels stage. Int J Life Cycle Assess 16:454–464.
[55] Stahl, W. and Stevens, R. (1992) Fuel-alcohol permeation rates of fluoroelastomers fluoroplastics, and other fuel resistant materials. SAE

Technical Paper 920163. Referred to in Kassel (2006) An Environmental Perspective: EPA’s RFS Proposal.

[56] Szybist, J.P., Youngquist, A.D., Baronet, T.L., Storey, J.M., Moore, W.R., Foster, M. and Confer, K. (2011) Ethanol Blends and Engine Operating Strategy Effects on Light-Duty Spark-Ignition Engine Particle Emissions. Energy & Fuels (2011), 25(11), 4977-4985. DOI:10.1021/ef201127y

[57] US EPA (2007) 40 CFR Parts 59, 80, 85, and 86, Control of Hazardous Air Pollutants From Mobile Sources. Final Rule. 26 February 2007.

[58] US EPA IRIS (2010) Integrated Risk Information System (IRIS). http://www.epa.gov/IRIS/. Data as of September 2010.

[59] Westerholm, R., Ahlvik, P. and Karlsson, H.L. (2008) An exhaust characterization study based on regulated and unregulated tailpipe and evaporative emissions from bi-fuel and flexi-fuel light-duty passenger cars fuelled by petrol (E5), bioethanol (E70, E85) and biogas tested at ambient temperatures of +22 °C and 7 °C. Final Report to the Swedish Road Administration, March 2008.

[60] Winkler, A., Eyssler, A., Magli, A., Liati, A., Dimopoulos, E.P., Bach, C. (2013) Fuel impact on the aging of TWC's under real driving conditions. Fuel (2013), 111, 855-864. DOI:10.1016/j.fuel.2013.04.014

[61] Winther, M., Møller, F. and Jensen, T. C. Emission consequences of introducing bio ethanol as a fuel for gasoline cars. Atmospheric Environment, Volume 55, August 2012, Pages 144–153.

[62] Yang, Y., Bae, J., Kim, J. and Suh, S. (2012) Replacing Gasoline with Corn Ethanol Results in Significant Environmental Problem-Shifting. Environ. Sci. Technol. 2012, 46, 3671-3678. doi: 10.1021/es203641p

[63] Yanowitz, J. and McCormick, R. (2009) Effect of E85 on tailpipe emissions from light-duty vehicles. J. Air & Waste Manage. Assoc. 59(2009)172–182.

[64] Mamakos, A., and U. Manfredi, 2012. Physical characteristics of exhaust particle emissions from late technology gasoline vehicles. JRC Scientific and Policy Reports, EUR 25302 EN, doi:10.2788/32371.

[65] Szybist J., Youngquist A., Barone T., Storey J., Moore W., Foster M. and Confer K. (2011). Ethanol Blends and Engine Operating Strategy Effects on Light-Duty Spark-Ignition Engine Particle Emissions. Energy & Fuels, 25: 4977–4985.

[66] Chan, T. W.; Meloche, E.; Kubsh, J.; Brezny, R.; Black Carbon Emissions in Gasoline Exhaust and a Reduction Alternative with a Gasoline Particulate Filter. Environ. Sci. Technol. 2014 Article ASAP. (web) April 23, 2014.

[67] ERMS Report #12-13 2012 Mazda 3 GASOLINE DIRECT INJECTION/ETHANOL BLENDS CAMPAIGN: ecoTECHNOLOGY for Vehicles II Program

[68] ERMS Report #12-16 ECOTECHNOLOGY FOR VEHICLES II PROGRAM, GASOLINE DIRECT INJECTION/ETHANOL BLENDS CAMPAIGN - Kias

[69] Rutten G A, Burtner C W J, Visser H, et al. The Determination of aldehydes in the exhaust gases of LPG fulled engines. Chromatographia, 1998(26): 274-280

[70] Robert Edwards, et al. Well-to-Wheels Analysis of Future Automotive Fuels and Powertrains in the European Context. SAE Paper 2004: 2004-01-1924

[71] Sergio M C, Graciela A. Carbonyl emissions in diesel and biodiesel exhaust. Atmospheric Environment, 2007, 41: 5436-5441

[72] Kenichi ITO, Toshiaki YANO, Ryo NAGASAKA. Unburned Methanol and Formaldehyde in Exhaust Gases from a Methanol Fueled S.I. Engine. Bulletin of the JSME, 1982, 210(25): 1938-1944

[73] C H Schleyer, W J Koehl. Comparison of Gasoline and Methanol Vehicle Emissions Using VOC Reactivity. SAE Paper 1990: 902095

[74] Vaughan R. Burns, William J. Koehl, Jack D. Benson, et al. Emissions with Reformulated Gasoline and Methanol Blends in 1992 and 1993 Model Year Vehicles. SAE Paper 1994: 941969

[75] Kenneth J Kelly, Brent K Bailey, Timothy C Coburn, et al. FTP Emissions Test Results from Flexible-Fuel Methanol Dodge Spirits and Ford Econoline Vans. SAE Paper 1996: 961090

[76] Lynd L R. Overview and Evaluation of Fuel Ethanol from Cellulosic Biomass: Technology, Economics, the Environment, and Policy. Annual Review of Energy and the Environment, 1996, 21: 403-465

[77] Kar K, Cheng W K. Speciated Engine-Out Organic Gas Emissions from a PFI-SI Engine Operating on Ethanol/Gasoline Mixtures. SAE Paper 2009-01-2673

[78] Zervas E, Montagne X, Lahaye J. Emission of alcohols and carbonyl compounds from a spark ignition engine: influence of fuel and air/ fuel equivalence ratio. Environ. Sci. Technol., 2002,36(11): 2414-2421

[79] Ecotraffic. (2006). INTROMET - Introduction of methanol as motor fuel. Eskilstuna: The Swedish Energy Authority.

[80] Bertilsson, & Egebäck. (1978). Comparative emission tests on vehicles fuelled with gasoline and gasoline mixed with methanol. Automotive emissions group. Studsvik and SMAB, BIL-99, 1978-02-01.

[81] Bertilsson, B. (1983). Environmental risk in handling alternative fuels, In Swedish.

[82] Britt-Marie Bertilsson et al., K.-E. E. (1978-02-01). Comparative emission tests on vehicles fuelled with gasoline and gasoline mixed with methanol. Studsvik: Automotive emissions group Studsvik, and SMAB, BIL-99.

[83] Aakko-Saksa, P. Murtonen, T., Roslund, P., Koponen, P., Nuottimäki, J., Karjalainen, P., Rönkkö, T., Timonen, H., Saarikoski, S. and Hillamo, R. Research on Unregulated Pollutants Emissions of Vehicles Fuelled with Alcohol Alternative Fuels - VTT's contribution to the IEA-AMF Annex 44. 2014, Research Report: VTT-R-03970-14.

[84] Aakko-Saksa, P., Murtonen, T., Koponen, P., Lehtoranta, K., Roslund, P., Karjalainen, P., Rönkkö, T., Timonen, H., Saarikoski, S., Hillamo, R. Nitrogen containing exhaust emissions for consideration in the aerosol research. Aerosol Technology, 2015, 15 - 17 June 2015, Tampere, Finland.

[85] Karjalainen, P., Timonen, H., Saukko, E., Kuuluvainen, H., Saarikoski, S., Aakko-Saksa, P., Murtonen, T., Dal Maso, M., Ahlberg, E., Svenningsson, B., Brune, W. H., Hillamo, R., Keskinen, J. and Rönkkö, T. Time-resolved characterization of primary and secondary particle emissions of a modern gasoline passenger car. Atmos. Chem. Phys. Discuss., 2015, 15: 33253-33282.

[86] Karjalainen, P., Arffman, A., Murtonen, T., Aakko-Saksa, P., Pirjola, L., Niemi, S., Keskinen, J. and Rönkkö, T. Real-time exhaust particle measurements with a high-resolution low-pressure cascade impactor. 2015, 19th ETH Conference on Combustion Generated Nanoparticles, June 28th - July 1st, 2015, ETH Zentrum, Zürich, Switzerland, 015_ETH-NPC-19.