

Measurement Methodologies for Hydrocarbons, Ethanol and Aldehyde Emissions from Ethanol Fuelled Vehicles

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ABSTRACT

Alternative fuelled vehicles are a growing market, and emission performance of these vehicles should be thoroughly investigated. The emission legislation is however very diversified in different countries; a short summary of the legislation in the EU, the USA and Brazil is presented in this study. In the EU regulations, everything measured with the FID (Flame Ionization Detector) is treated as hydrocarbon emissions. In the USA the alcohols and aldehydes are measured and reported separately from hydrocarbons. In Brazil, the alcohol part can be measured separately on voluntary basis. The influence of some of these differences has been further investigated in this report.

Results from two related studies are presented. The FID response for ethanol was investigated and emission testing of an E85 fuelled FFV (Flex Fuel Vehicle) was performed.

The FID sensitivity at two different detector temperatures – 113°C (as stated by the US EPA when testing alcohol fuelled vehicles) and 190°C (often used as default setting in the EU) – were investigated showing a higher FID response at 113°C. The response curve shows a slow response due to adsorption of ethanol in the measurement system.

One FFV fuelled with E85 was tested on chassis dynamometer at two ambient temperatures: +22°C and –7°C. The ethanol emissions were analyzed with FTIR and sampled in impingers (standardized method approved in the USA). The acetaldehyde emissions were analyzed with FTIR and sampled in DNPH(2,4-dinitrophenyl hydrazine)-cartridges

(standardized method approved in the USA). The FTIR provides second-by-second data which showed that high levels of unburned ethanol were emitted during the cold start phase. Comparison between the FTIR results and methods standardized in the USA were performed.

The percentage distribution of some of the components included in the total hydrocarbons measured by the FID was investigated, and comparison between tests performed at the two different ambient temperatures can be made. The proportion of unburned ethanol increased at cold climate testing - from 24% at +22°C up to 53% at –7°C.

INTRODUCTION

The importance of finding alternatives for fossil fuels is unquestionable. To be able to reduce the emissions of CO₂, the development of renewable fuels and technology are of most interest. The natural resources of feedstock for production of renewable fuels that can be produced within the country should be investigated, and used in the first place. As one of the alternatives, the interest of using alcohols, and especially ethanol, as vehicle fuel is high in Sweden. The advantages are many, such as; being renewable, the ethanol has the potential to be produced within the country and it is easily mixed with petrol. Besides the use of alternative fuels in combustion engines, the environmental impact of the production processes is also of importance.

In 2008, alternatively fuelled vehicles constituted almost 25% of new cars sold in Sweden. By the end of 2008 almost 4% of the vehicle fleet in operation in Sweden was alternatively fuelled vehicles. Of the alternatively fuelled vehicles, almost

70% constitutes of FFVs fuelled with ethanol (E85). In Sweden there are about 3500 tank filling stations, and approximately 1300 of these supplies E85. [Figure 1](#) shows the growing interest for ethanol fuelled FFVs in Sweden. The rapid increase of alternative fuelled vehicles is mainly due to various economic incentives. [1]

See [Figure 1](#) after last section of paper

Apart from Sweden, alcohol fuels are also considered to be a substantial part of the alternative fuel market in Brazil and USA. In the USA there are about 2000 tank filling stations for E85, most of these are located in the midwest region. In Brazil the production of ethanol is extensive and Brazil is the largest exporter of ethanol fuel. Ethanol fuelled vehicles is commonly used, and all petrol sold is blended with 20-25% ethanol. Almost 90% of the new cars sold in Brazil are FFVs.

With the growing interest it is of most importance to investigate and validate the emission performance of vehicles fuelled with alcohols. The focus in this report is on measurement and calculation of hydrocarbon, alcohol and aldehyde emissions from an E85 fuelled vehicle.

The emission regulations in different countries have different ways to treat alcohol fuelled vehicles. From a European point of view, it is interesting to study the regulations in USA and Brazil concerning these types of vehicles. A short summary of the regulations in EU, USA and Brazil is included in this study. When alcohols are used as blending components in petrol, uncombusted alcohols from the fuel are emitted in the exhaust in various amounts. When a FID is used to measure hydrocarbons, the uncombusted alcohol will be included in the measurement. In the EU regulations everything measured with a FID is treated as hydrocarbon emissions. In the US regulations, the alcohol content is measured separately, and the FID measurement is adjusted for the alcohol part. In Brazil the vehicle manufacturer has the possibility to choose between these two methods.

Before the introduction of the Euro 5 emission standard for light duty vehicles, there were no special requirements for FFVs in EU, and the mandated testing was performed using only reference fuel. In the Euro 5 emission standard testing is required to be performed on reference fuel meeting specifications both for petrol and ethanol (E85). To calculate the mass emissions a different density for HC is used for E85 fuel leading to approximately 50% higher HC emissions, only due to calculation. A worst case scenario would be that, due to legislation, the development of alternatively fuelled vehicles is delayed.

In this report results from two studies are presented. In the first part, the FID response to ethanol has been investigated. In the second part, results from vehicle tests from an FFV fuelled with E85 are presented.

EMISSION REGULATIONS

EU

In the certification process of the Euro 4 and earlier regulations [2], alcohol fuelled FFVs were not required to be tested with the alternative fuel. The tests were performed using “reference”-petrol only, and there were no differences in the evaluation of the emissions. In Euro 5, applicable from September 2009, this has been changed. The FFVs are to be tested with both reference specifications of petrol as well as E85 fuels according to the Type 1 test in the regulations. The Type 1 test is defined as “Verifying average exhaust emissions at ambient conditions”, where the vehicle is tested according to the NEDC test cycle at ambient temperature. From 2011, Type 6 testing at low ambient temperature will be introduced. Type 6 testing will possibly imply another specification for the reference ethanol (E75 or “E85 winter quality”). The test requirements for FFVs are presented in [Table 1](#).

See [Table 1](#) after last section of paper

In EU regulations the total emissions of hydrocarbons and non-methane hydrocarbons are regulated. The mandated measurement procedure is by using a FID-instrument, calibrated with propane in synthetic air. Flexible fuelled vehicles are tested according to the same procedure as petrol fuelled vehicles. There are no specifications for FID detector temperature for positive ignition vehicles. For compression ignition vehicles the FID detector together with valves, pipework etc must be heated to 463 K (190°C) which is defined as HFID (Heated FID). It is therefore common that test laboratories use 190°C as default setting for the detector temperature.

The density used for calculating the mass emissions of hydrocarbons are higher for E85 due to the difference in molecular weight, which leads to an increase of approximately 50%.

The following densities for calculation of hydrocarbon mass emissions are applicable for petrol and E85:

Euro 4:

For petrol (C₁H_{1,85}) $d = 0,619 \text{ g/dm}^3$

Euro 5:

For petrol (C₁H_{1,89}O_{0,016}) $d = 0,631 \text{ g/dm}^3$

For ethanol (E85) (C₁H_{2,74}O_{0,385}) $d = 0,932 \text{ g/dm}^3$

The effect of the change in density for calculating hydrocarbon mass emissions, when the vehicle is operated with E85, is illustrated in [Figure 2](#).



See [Figure 2](#) after last section of paper

USA

The federal emission standards (set up by US EPA) must be met by all new vehicles sold in the US. California has however been granted, by the Clean Air Act, to adopt its own emission standards which are stricter than the federal standards. These standards are set up by the Californian Air Resource Board (CARB). Some other states have followed and adopted the Californian standards.

The FTP75 test cycle is used for legislative testing of alcohol fuelled vehicles. The hydrocarbon, alcohol and aldehyde emissions are included in NMOG (NonMethane Organic Gases), which is regulated. The definition of NMOG is the emissions of NonMethane Hydrocarbons (NMHC) and oxygenated hydrocarbons. The weighted mass emissions of NMOG are the sum of total emissions of NMHC, alcohols and aldehydes. NMHC is measured with FID, and alcohols and aldehydes are measured separately. Alcohols are sampled in impingers or measured with Photo Acoustic Sensor (PAS). When sampling is performed in impingers, the distilled water (containing the alcohols) is analyzed by GC (Gas Chromatography). Aldehydes are sampled in DNPH-cartridges which are analyzed by HPLC (High Performance Liquid Chromatography). [4]

The alcohols and aldehydes contribute to the NMHC emissions measured by the FID. To be able to subtract these components from the FID-NMHC, response factors are established for alcohols and aldehydes respectively. By applying the response factor to the (separately measured) alcohols and aldehydes, their respective contribution to the FID-NMHC can be removed.

The FID detector temperature should be set to 113 °C for alcohol fuelled vehicles (instead of 190 °C which is used for petrol and diesel fuelled vehicles). This is based on the higher water vapour of methanol, and the fact that methanol can undergo decomposition reactions if the oven is too hot [5]. The difference in FID sensitivity at different temperatures is further discussed in a separate part of this report.

BRAZIL

Brazil has an extensive production of ethanol, and ethanol fuelled vehicles is commonly used. All petrol sold is blended with 20-25% ethanol, and almost nine of every ten new cars sold in the Brazilian market are Flex Fuelled Vehicles. The content of ethanol in the fuel varies, and the FFVs on the Brazilian market are capable of running on fuels with up to 100% hydrated ethanol (93% ethanol, 7% water) [6].

NMHC is regulated, where the methane part is subtracted. The vehicle manufacturer has the right to measure the unburned ethanol separately (by sampling in impingers) and

discount this value from the NMHC emissions. The FID response factor for ethanol is established, which is used to remove the ethanol part from the NMHC emissions. In this case the calculations are similar to the US EPA. [7] The difference is however that the subtracted ethanol part is not included later on (as in the US regulations, where ethanol is included in NMOG).

See [Figure 3](#) after last section of paper

FID RESPONSE TO ETHANOL

In the European regulation, the FID is assumed to respond to all hydrocarbons identically as it responds to propane in determining the concentration of carbon atoms in a gas sample.

In the US EPA regulation, the difference in response is taken into account and response factors are established for oxygenated hydrocarbons and methane. The FID measurements are thereby corrected for the presence of these compounds in the measured exhaust. Measured response factors are determined for each compound known to be present, and to affect, the FID response.

Response factors should be measured directly on the FID instrument being used for HC measurement. Note that FID response to ethanol may be slow due to ethanol adsorption on walls of supply tubing [8,9]. This should be taken into account when determining FID response and sample time for THC measurement, to be certain that an accurate response to ethanol is obtained.

According to US EPA, the FID response factor to methanol is calculated as follows:

$$r = \text{FIDppm} / \text{SAMppm}$$

$$r = \text{FID response factor}$$

$$\text{FIDppm} = \text{FID reading in ppmC}$$

$$\text{SAMppm} = \text{methanol concentration in the sample, or gas bottle, in ppmC}$$

In the EU regulations, there are no specifications for FID detector temperature for spark ignition vehicles. As stated earlier in this report 190 °C is commonly used as default setting.

In the US EPA regulation the FID detector must be set to 113 °C when testing an alcohol-fuelled vehicle.

We have studied the influence of FID detector temperature and compared 113 °C with 190 °C. This comparison is presented in [Figure 4](#).

EXPERIMENTAL AND RESULTS

In order to examine the response factors of a FID instrument an experimental study was performed. A gas bottle (with known concentration of ethanol) was connected to the sampling bag inlet, and the sampling bag was filled with the gas. The FID instrument was thereafter used to analyze the sampling bag. No time limit was set, all gas in the bag was analyzed.

The FID was calibrated with propane according to standard procedure.

See [Figure 4](#) after last section of paper

From [Figure 4](#) it is notable that the FID sensitivity is very different for the two temperatures.

The response curves show the same pattern, with a considerably slow response, which is due to ethanol adsorption in the measurement system. The maximum concentration is not reached until after 5 minutes of analyzing. This adsorption characteristic of ethanol is further discussed in [9], together with the urge to develop and specify test procedures for ethanol fuelled vehicles based on the specific characteristics of the ethanol content in the emissions.

If the concentration after a sampling time of 90 seconds is used, the response factors for the different temperatures are:

Rf: 0,67 (113 °C)

Rf: 0,48 (190 °C)

The low FID-response for ethanol is in accordance with earlier studies [10,11].

VEHICLE TESTS

As a complement to the more theoretical study of response factors of a FID instrument, vehicle tests were also performed.

EXPERIMENTAL

Vehicle and fuels

A Skoda Octavia FFV, certified to the Euro 4 emission standard, was used in the testing. The road load curve for the vehicle was kindly supplied by the vehicle manufacturer. Please note that the objection is to analyze the emissions of HC, ethanol and acetaldehyde when fuelled with E85. The test results can not be compared to the Euro 4 emission standard since no tests were performed with the certification fuel.

Table 2. Vehicle specification

Make	Skoda
Model	Octavia 1,6
Model year	2008
Emission standard	Euro 4
Odometer (km)	9903
Inertia mass (kg)	1350
Displacement (cm3)	1595
Power (kW)	75
Gearbox	M5
Fuel	Petrol / E85

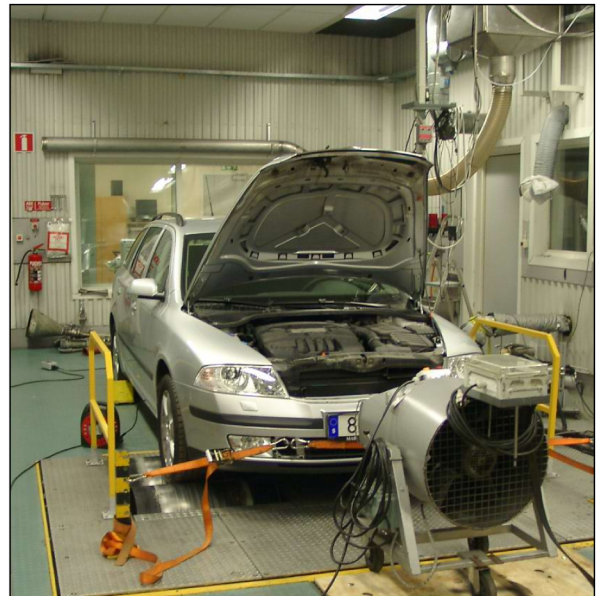


Figure 5. The test vehicle on the chassis dynamometer.

For the 22 °C tests E85 commercial available fuel was used, for -7 °C tests E75 commercial available fuel was used.

Test program

The emission tests were performed using the New European Driving cycle (NEDC) which is the legislative test cycle used for emission certification of light duty vehicles in the EU. The cycle is shown in [Figure 6](#).

See [Figure 6](#) after last section of paper

The NEDC cycle can be divided into different parts. The first part of the cycle includes four identical parts, representing the Urban Driving Cycle (UDC). The UDC can be further divided into two parts, UDC1 and UDC2. This enables one to look at cold start performance compared to the warm engine. The UDC part is followed by a part with higher speed, the Extra Urban Driving Cycle (EUDC). The total length of the test cycle is 1180 sec.

Tests were performed at the two ambient temperatures used for certification of light duty vehicles operated on petrol from 2009, and on E85 from 2011 – 22 °C and –7 °C.

Measurement methods

Testing was performed at the laboratories of AVL MTC, Sweden and VTT, Finland.

AVL MTC

The vehicle was tested on an electric Clayton DC500 double 500 mm roller chassis dynamometer. The dynamometer settings were applied according to the EU regulations (using the load curve supplied by the manufacturer). A Horiba CVS-9300T Constant Volume Sampler was used. Cleaned and HEPA filtered test cell air is introduced into the exhaust stream for dilution. The dilution tunnel flow rate is controlled by the use of a 9 m³/min critical venturi.

The regulated emissions were measured according to the standard EU test procedure using a Horiba Mexa 9400D. The diluted exhausts were sampled in three bags for the different parts of the NEDC test cycle (UDC1, UDC2 and EUDC). Among the regulated emissions, only HC emissions will be presented in this report. The HC emissions were measured with FID. The detector temperature was set to 190°C, which is the regular FID setting at AVL MTC. The FID was calibrated with propane.

The ethanol emissions were analyzed with FTIR (Fourier Transform InfraRed) (AVL SESAM) and sampled in impingers. The FTIR provides second-by-second data. The impingers samples through the total cycle, and the distilled water (containing the alcohol) was sent for analysis to an external laboratory.

The acetaldehyde emissions were sampled in DNPH-cartridges through the total cycle. Two cartridges in series were used. After sampling the cartridges were sent for analysis to an external laboratory.

Three identical tests (triplicate) were performed for each temperature setting.

VTT

The vehicle was tested on a FroudeConsine single roller chassis dynamometer, with a diameter of 1,25 m. A Constant Volume Sampler (Pierburg 12.5 WT) was used in the study.

A Pierburg AMA 2000 was used for measurement of regulated emissions. The diluted exhausts were sampled in three bags for the different parts of the NEDC test cycle.

The ethanol emissions were analyzed with FTIR (Gasmeter CR2000) and sampled in impingers.

The acetaldehyde emissions were analyzed with FTIR and sampled in DNPH cartridges.

Two identical tests (duplicate) were performed for each temperature setting.

EMISSION TEST RESULTS

Please note that the scales are different in the diagrams.

The focus in this part of the report is on emissions of hydrocarbons, ethanol and acetaldehyde from FFVs fuelled with E85 (E75 for cold climate testing).

In the exhausts from an FFV fuelled with ethanol, unburned ethanol and acetaldehyde will be present [10,11]. Startability of an FFV engine is much dependent upon the presence of the petrol part of the E85 fuel. In order to improve the start, extra fuel has therefore to be injected during the start-up phase allowing more petrol to take part in the combustion. The level of emitted ethanol is dependent on the driving cycle; if the driving cycle starts from a cold engine (which is the case for the NEDC test cycle) the levels will be high during the cold start phase. The high emissions of ethanol at cold start are also discussed in [9,11]. To show this, second-by-second results measured by FTIR is presented in [Fig. 7](#) and [Fig. 9](#) respectively. Since FTIR is not a standardized method, the test results are followed by a comparison between FTIR results and a standardized method.

Ethanol

The ethanol emissions were analyzed by FTIR providing second-by-second data, and sampled in impingers over the total cycle. The FTIR results gives a good view of what happens during the start of the engine, see [Figure 7](#). Very high levels of ethanol emissions are emitted during the first part of the test cycle, and the emission levels are clearly temperature dependent.

See [Figure 7](#) after last section of paper

FTIR is not a standardized method for analyzing ethanol, and the ethanol emissions were also sampled in impingers. Since the impinger sampling (the distilled water was further