

ENGINE EXHAUST ALDEHYDE MEASUREMENT USING GAS CHROMATOGRAPHY

Paola Helena Barros Zárante

PUC Minas, Av. Dom José Gaspar, 500, 30535-610, Belo Horizonte, MG, Brazil
paolabarros@hotmail.com

Theles de Oliveira Costa

PUC Minas, Av. Dom José Gaspar, 500, 30535-610, Belo Horizonte, MG, Brazil
theles.costa@ig.com.br

Pablo Carmélio Cardoso de Albuquerque

PUC Minas, Av. Dom José Gaspar, 500, 30535-610, Belo Horizonte, MG, Brazil
pablomech@ibest.com.br

José Ricardo Sodré

PUC Minas, Av. Dom José Gaspar, 500, 30535-610, Belo Horizonte, MG, Brazil
ricardo@pucminas.br

Abstract. *This work describes new method for measurement of aldehyde emissions from internal combustion engines. The method employs gas chromatography with flame ionization detector analyzer, with the sample gas collected straight from the exhaust pipe. Formaldehyde and acetaldehyde were identified and quantified for a production, 1.4-liter spark-ignition engine, fueled by hydrous ethanol. The testes were carried out in a bench test dynamometer, in the engine speed range from 2000 to 4000 rev/min. from oxidation of unburned ethanol, methane or ethane. The retention times of formaldehyde and acetaldehyde were consistent for all tested condition. The measured concentrations did not define a trend for aldehyde emissions variation with engine speed. The results demonstrate the gas chromatography method to be an interesting alternative to the conventional liquid chromatography method for engine exhaust aldehydes qualification and quantification.*

Keywords: *aldehydes, ethanol, emissions, internal combustion engines, gas chromatography*

1. INTRODUCTION

The incomplete combustion of ethanol fuel releases high concentrations of aldehydes and alcohols in the exhaust of spark ignition engines, with harmful toxic characteristics and intense photochemical activity. Aldehydes are highly reactive organic compounds characterized by the functional group aldoxile (CHO). Among the several types of existing aldehydes, only the ones found in gaseous state are considered pollutant emissions: formaldehyde (CH₂O) and acetaldehyde (C₂H₄O). Engines operating on methanol release higher concentrations of exhaust formaldehyde and, for when ethanol is used as fuel, acetaldehyde predominates.

The internal combustion engines controlled pollutants are carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_x) and aldehydes (CHO). In engines fueled with alcohol exhaust aldehyde (CHO) concentration reaches important levels, thus receives a special attention. Compared with gasoline, aldehyde emissions reach higher exhaust concentrations for alcohol fuels due to presence in their molecules of the functional group hydroxile (OH).

The control of regulated pollutant emissions from internal combustion engines exhaust was initiated in Brazil with the institutionalization of PROCONVE – Vehicle Air Pollution Control Program – in 1986, through the CONAMA (National Environment Council) resolution number 18/86, that established the vehicle emissions limits. Brazil uses hydrous ethanol and gasoline plus 20–25 % of anhydrous ethanol as fuels, which produce aldehydes as singular pollutants. Aldehydes are formed in the intermediate stages of alcohol and hydrocarbons oxidation and their maximum limits were introduced only in 1992.

Knowledge of aldehydes formation process is fundamental to determine their emission levels variation as a function of engine geometric and performance parameters, allowing for the right setting of the engine control system. It is calibrated for best engine performance and least exhaust emissions levels, including aldehyde concentration.

Regulated exhaust aldehydes are commonly measured by the DNPH-HPLC (dinitrophenylhydrazine and high-performance liquid chromatography) method. This method is highly reliable, but requires many steps to the final analysis, which is available long after exhaust sample collection. Thus, the objective of this work is to measure engine exhaust aldehyde concentration using a non-conventional gas chromatography method. While the relatively low aldehyde concentration is harder to be analyzed by gas chromatography, this method is rather straightforward in comparison to the DNPH-HPLC method, and can become an interesting alternative.

2. LITERATURE REVIEW

2.1 Aldehyde formation mechanism

Formaldehydes are found in chamber unburned gases, under detonation conditions (Withrow and Rasswuller, 1934). These gases are not responsible for exhaust aldehyde, being consumed by the flame front in elapsing combustion. Browning and Pefley (1979) computational studies indicate that aldehydes do not survive into unburned gases during combustion inside the cylinder. The exhaust aldehydes are formed as intermediate species from post-combustion oxidation of unburned methanol.

Browning and Pefley (1977a; 1977b) used a detailed kinetic reaction mechanism to study aldehyde formation in unburned gases area next to combustion chamber walls under some conditions. They verified that aldehyde concentration increases at flame extinction, but that does not correspond to the concentration found in exhaust. Flow reactor studies had shown that aldehyde formation initiates after the end of combustion. In subsequent studies Browning and Pefley (1979) has shown that aldehyde formation was not complete by the end of combustion, when flame diffusion quickly removes most of the unburned fuel, without significant aldehyde formation. Exhaust aldehyde formation was examined analytically (Browning and Pefley, 1980), for a range of engine operation conditions, varying mixture equivalence ratio, compression ratio, ignition angle and rotational speed.

Ito and Yano (1980) described another chemical kinetics model to explain the initial aldehyde formation mechanism for spark ignition engines fueled with methanol. The model includes a reaction that became important in an exhaust system containing a large NO_x quantity in a temperature range from 600 to 1000 K. The model was validated by experiments in a warm reaction tube adapted to the exhaust door. Calculated results of unburned methanol and formaldehyde concentration were close to reactor tube measurements under some temperature and exposition time conditions. Formaldehyde levels grew when oxidation of unburned methanol did not progress, reaching a minimum when methanol exposition time in the reactor was increased.

Särner et al. (2005) made a formaldehyde and toluene simultaneous image register study by laser inductive fluorescence (LIF). Measurements were carried out with initial and final injection at 35 and 250 BTDC (before top dead center), respectively. Mixtures of n-heptane and iso-octane were used as fuels and toluene as fluorescent examiner. The experiments involved two lasers and two photographic machines. Formaldehyde appears as intermediate species in hydrocarbon combustion, being formed in low temperature reactions at the beginning of combustion and consumed after the end of it.

Using high performance liquid chromatography (HPLC), Sluder et al. (2004) had verified that diesel engine aldehyde emissions diminished with the increase of exhaust gas recirculation (EGR). A possible explanation is the adhesion of aldehydes to emissions of growing particulates that stopped them to be trapped in DNPH cartridges for analysis. It was also noticed that emission levels of higher molecular weight aldehydes did not drop as it happened to acetaldehyde and formaldehyde. Aldehyde formation is an indication of hydrocarbon fuel partial oxidation. Aldehyde emissions increase for a low NO_x and particulate (PM) combustion regime. This increase was particularly high for formaldehyde and acetaldehyde, but it was also observed for benzaldehyde, propionaldehyde and acrolein. High aldehyde emissions are consistent with low temperature combustion regime.

2.2 Influence of engine geometric parameters

Variations on air/fuel ratio essentially influence oxygen concentration and gas temperature in the exhaust, both potentially important for aldehyde reactions. Ayyasamy et al. (1981) observed that around stoichiometric fuel/air ratio the high temperature combustion produces a minimum aldehyde amount. In this condition the flame speed reaches a maximum, optimizing combustion and reducing flame extinction inside the combustion chamber next to the walls. Aldehyde concentration increases when the mixture becomes very rich or very lean.

Analyzing the compression ratio effects, Bernhardt (1977) verified that aldehyde emissions diminished when compression ratio was increased. Using ethanol as fuel, Brinckman (1977) observed that aldehyde emissions growth with compression ratio increase. The main reason for this aldehyde emission increase was exhaust temperature reduction, as a consequence of a faster combustion that occurs with high compression ratios. According to Poschinger and Kramer (1979), the influence of compression ratio on aldehydes is not uniform. For lean mixtures, aldehyde concentration always increases with high compression ratio. The unburned fuel partial oxidation in the exhaust pipe is more complete at high temperatures and low compression ratios (Ito and Yano, 1980).

Ayyasamy et al. (1981) verified aldehyde emission level increase for a delayed ignition angle using methanol as fuel. With gasoline, the authors did not observe significant changes in aldehyde emissions with the variation of ignition angle. These results agree with those by Pischinger and Kramer (1979). With the spark delayed less time is allowed for combustion completion, contributing to aldehyde emissions increase (Ayyasamy et al. 1981).

Amaral and Sodré (2001) studied the effects of engine geometric parameters on aldehyde emissions. Variation of intake and exhaust valves opening, compression ratio, and gap between the spark plug electrodes were investigated through experiments in a vehicle with a 1.0-liter engine fueled with ethanol. It was verified that higher compression

ratios reduce simultaneously CO and HC emissions, while keeping unchanged NO_x concentration levels. Other studies by Amaral and Sodré (2002) showed the effects of the following engine operation parameters on aldehyde emissions: mixture equivalence ratio, additional air used for decelerations, fuel interruptions on decelerations and gear change. It was concluded that aldehyde emission reduction could be reached for gear changes at lower vehicle speeds and richer air/fuel mixtures.

2.3 Fuel effects on aldehyde emissions

Methanol and ethanol tests had shown NO_x concentration reduction when compared with gasoline while CO and HC emissions remain unaltered. Aldehyde emissions for methanol and ethanol increase from 2 to 10 times when compared with gasoline (Huang et al. 1998; Sales e Sodré, 2003).

Carrol et al. (1990) verified the emissions produced by a diesel engine urban bus fueled with methanol and ethanol mixtures as an alternative fuel. Using some configurations and alcohol mixtures, they measured aldehydes and other pollutants. It was verified that the emission limits for the biggest methanol volumetric amounts produce aldehyde, acetaldehyde and formaldehyde concentrations above the limits allowed by emission control federal laws, mostly in cold starts. Using pure ethanol they verified just the presence of formaldehyde and other pollutants, not having measurable amounts of acetaldehydes. For other mixture proportions, concentrations of these two aldehydes were verified in relevant amounts.

Sandquist et al. (2001) verified in a stratified charge direct injection engine vehicle that addition of ethanol in few volumetric concentrations in commercial gasoline does not provoke significant alterations in HC, CO and NO_x. However, aldehyde emissions are raised from 2 to 3 times when 5% of ethanol is added to gasoline.

Hirota et al. (1990) researched the use of methanol and gasoline mixtures on a production engine. The authors compared aldehyde emissions for pure gasoline and a blend of 15% gasoline and 85% methanol. The results showed an increase in formaldehyde emissions for the fuel blend and a light reduction on CO and NO_x emission. It was concluded that using methanol in low concentrations reduces some pollutant emissions, however increases aldehyde emissions.

Aubin and Smith (2001) analyzed pollutant emissions using a mixture of 85% ethanol by volume with 15% gasoline. The experiments were carried out following FTP-75 emissions test standard, in a eight-cylinder pick up truck. Modifications in engine operating parameters were proposed to improve the performance and to reduce cold start emissions at steady state. The results obtained led to the conclusion that aldehyde concentration levels for ethanol-fuelled engines are high and need a catalytic converter to reduce their emissions. The results showed that using ethanol as fuel acetaldehyde concentration is higher than formaldehyde concentration.

Ouissek et al. (1991) investigated the use of ethanol as fuel for Brazilian market passenger vehicles. They evaluate the performance and emissions of 1.3, 1.6 and 2.0-liter engines used in commercial vehicles. For controlling aldehydes an adequate solution was the use of a three way catalyst, located next to the engine exhaust port.

Vicentini e Kronberger (2005) made a comparative analysis between two vehicles with flexible-fuel engine (gasoline and hydrous ethanol mixtures) and similar projected models for gasoline use only. The flexible-fuel technology was evaluated for driving, performance, vehicle speed recovery, exhaust emissions (THC, CO, NO_x and aldehydes), fuel consumption, and maintenance costs. Regular gasoline with 22% by volume of anhydrous ethanol, standard hydrous ethanol with 6.8% by volume of water, a blend of 50% by volume of regular gasoline plus 50% of hydrous ethanol (resulting in a 39% gasoline, 57% ethanol and 3% water) were used as fuels. It was verified that the increase of mixture hydrous ethanol content results in formaldehyde and acetaldehyde emissions ten times higher than with regular gasoline use. Based on the results, it was concluded that flexible-fuel technology reaches satisfactory performance and good driving characteristics, however the high aldehyde emission levels must be reevaluated concerning to environmental impact and air quality in great centers.

Merrit et al. (2005) made a comparative study on regulated and non-regulated exhaust emissions in diesel engine off-road vehicles fueled with ethanol and diesel oil mixtures. Two diesel oil samples (400 ppm of sulfur) and three ethanol-diesel oil mixtures with 7,7%, 10% e 15% of ethanol were used. Three off-road vehicles with 6.8, 8.1 and 12.5-liter engines with different fuel injection systems were used. Total HC, NO_x, CO, CO₂ and particulate matter (PM) were analyzed to quantify individual hydrocarbons, aldehydes, ketones, alcohols, polynuclear aromatic hydrocarbons (PAH), 1-nitropereno and soluble organic fraction (SOF) of particulate. Increasing ethanol concentration in the mixture produces higher acetaldehyde emissions, from 27% to 2.39 times.

3. EXPERIMENTAL METHODOLOGY

3.1 Dynamometer Tests

A production 1.4-liter flexible fuel spark ignition engine, with four in-line cylinders and compression ratio 10.35:1, was tested in a bench dynamometer for verification of aldehyde emissions. A hydraulic dynamometer was used, of 261 kW (350 hp) maximum power capacity and 6000 rev/min maximum rotational speed. The tests were carried out in accordance to NBR 1585 standard (ABNT, 1986) for measurement of engine performance in conditions of steady state

operation. Before starting the measurement at each tested condition, the engine was operated for at least 2 minutes until all instrument readings were stable. The measurements were carried out at 2000, 3000, and 4000 rev/min, representative of a spark ignition engine normal operation regime. The engine operating conditions were modified by varying the dynamometer load applied. During the tests the engine was fueled with hydrous ethanol, which produces aldehydes in larger amounts than gasoline. It was made possible, thus, to produce enough formaldehyde amounts so it can be easily identifiable by the gas chromatograph method, once, according to Swarin et al. (1992), this aldehyde produces low response signal to FID detector, used by the chromatograph.

The engine rotational speed was measured through a magnetic sensor and checked by a diagnosis equipment connected to the engine electronic control module. The exhaust temperature was monitored through a K-type thermocouple installed before the catalyst, next to the exhaust port. The experiments were performed in the Internal Combustion Engine Laboratory of PUC Minas.

3.2 Gas Chromatography Analysis

For aldehyde analysis (formaldehyde and acetaldehyde) a gas chromatograph was used. The chromatograph works with a center sample program, which can be configured in accordance to the analysis required. An electronic pneumatic control (EPC) allows for programming all pressures and flows in the method. Once fixed, the pressures and flows remain constant. For aldehyde and hydrocarbons analysis, the chromatograph is equipped with a flame ionization detector (FID). With the option of accumulative entrance, it can be used capillary columns to fixed resultant high resolution. The small oven allows for fast temperature increase of temperature and short cooling time without the need of a high voltage source.

An Agilent HP-INNOWax Column was used for aldehyde analysis. The column is based in polyethylene glycol (PEG), and is ideal to analyze polar combination and also a variety of combination of solvents and aromatics. The INNOWax column had an operation temperature limit of 270°C. The chromatograph oven temperature was programmed throughout the analysis in order to get a good separation of the analyzed compounds. The sample admitted on the chromatograph was collected directly from the engine exhaust system, next to the exhaust port. Inside the chromatograph the sample was transported through the column by gaseous hydrogen flow. The chromatograph response was stored by a dedicated computer program, including dates, peak times of retention, peak areas, peak type and calculated concentration. The chromatograph was calibrated for aldehydes and hydrocarbons analysis through chromatograms supplied by the manufacturer for the same equipment readiness. With similar column and equipment settings, formaldehyde and acetaldehyde were identified by the corresponding peaks arising at the same retention times shown by the manufacturer's chromatograms. The expected error associated to the species identification through this procedure is small. The chromatograph column specifications, supplied by the manufacturer, and adjusted parameters for aldehyde analysis are shown in Tab. 1. The manufacturer's chromatograms are shown by Figs. 1 and 2.

Table 1. Chromatograph settings for aldehyde analysis.

PARAMETER	SPECIFICATION
Column	DB-WAX
Column length	30 m
Internal column diameter	0,32 mm
Covering Thickness	0,5 µm
Carrying gas	Hydrogen
Carrying gas speed	36 cm/s a 35°C
Oven temperature	35°C for 10 min, 35-240°C a 120°/min, 240° for 10 min
Split	1:30
Injector temperature	200°C
Detector	FID
Detector temperature	300°C
Composition gas	Nitrogen
Composition gas flow	30ml/min

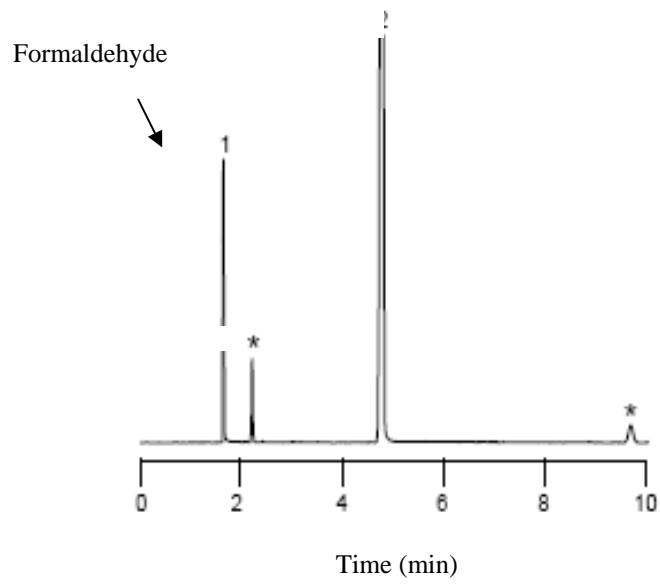


Figure 1. Typical chromatogram obtained for formaldehyde analysis using DB-WAX column. Source: Agilent

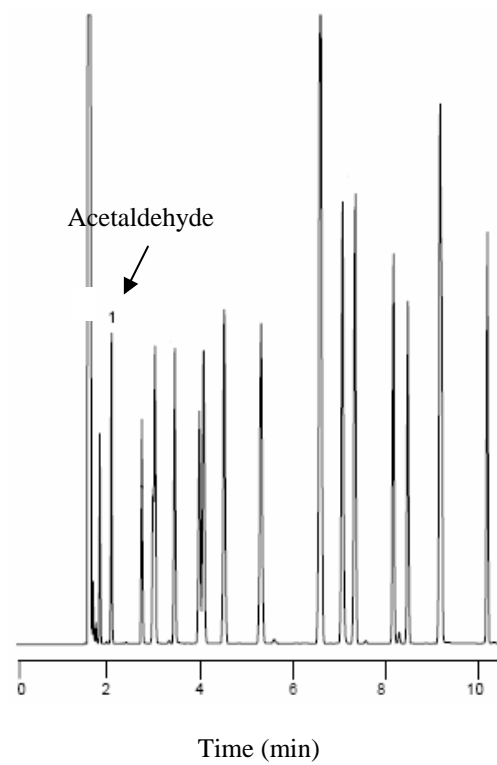


Figure 4 – Typical chromatogram obtained for acetaldehyde analysis using DB-WAX column. Source: Agilent

4. RESULTS AND DISCUSSIONS

The chromatograms obtained for ethanol fuel, formaldehyde and acetaldehyde are shown in Fig 3 to 6. Figure 3 shows the chromatographic analysis for hydrated ethanol injected in the quantity of 0.1 μl , with 1:30 split, using the DB-WAX column. Ethanol was released at 4.858 min retention time, with a known approximate concentration of 93.2% (Table 2). The liquid ethanol was injected through a syringe. Its identification was used to estimate the formaldehyde and acetaldehyde concentrations in the gaseous samples tests.

Fig. 4 shows the aldehyde analysis by gas chromatography using direct exhaust gas sampling at 2000 rev/min engine speed. Formaldehyde and acetaldehyde were released at 1.214 min and 1.605 min retention times, respectively. Considering 1999 ppm of unburned ethanol concentration, established by the peak area proportion to the chromatogram obtained when the liquid fuel was injected (see Fig. 3 and Table 2), formaldehyde and acetaldehyde estimated concentrations were 56 ppm and 181 ppm, respectively (Table 3).

Fig. 5 shows the chromatographic exhaust aldehyde gas analysis at the engine of 3000 rev/min. In this case, the retention times for formaldehyde and acetaldehyde were 1.216 min and 1.607 min, respectively. The estimated formaldehyde and acetaldehyde concentrations were 101 ppm and 212 ppm, respectively (Table 4).

Fig. 6 shows the obtained chromatogram for aldehyde analysis at the engine speed of 4000 rev/min. Formaldehyde showed a retention time of 1.212 min, whilst, for acetaldehyde, the retention time was 1.603 min. The estimated formaldehyde and acetaldehyde concentrations were 73 ppm and 104 ppm respectively (Table 5).

From Figs. 3 to 6, the retention times of the identified elements were consistent throughout all the engine speed range investigated. However, the concentrations found did not define a clear trend with variation of engine speed for any of the components. That was probably due to condensation of the heavier exhaust gas components in the connection of the heated sample line to the chromatograph inlet sample port. At the moment the sample line was connected the inlet sample port, the chromatograph inlet sample valve was closed, increasing the sample pressure and, thus, causing local condensation. That was dealt with by connecting the sample line to the inlet sample port just before the inlet sample valve opening. However, that was of difficult synchronization, and, together with the shortage of data obtained at this stage, prevents the formulation of conclusive statements about the influence of engine speed on aldehyde emissions. Further investigation involving a broader engine speed range and data collection is required to establish the aldehyde emissions trends.

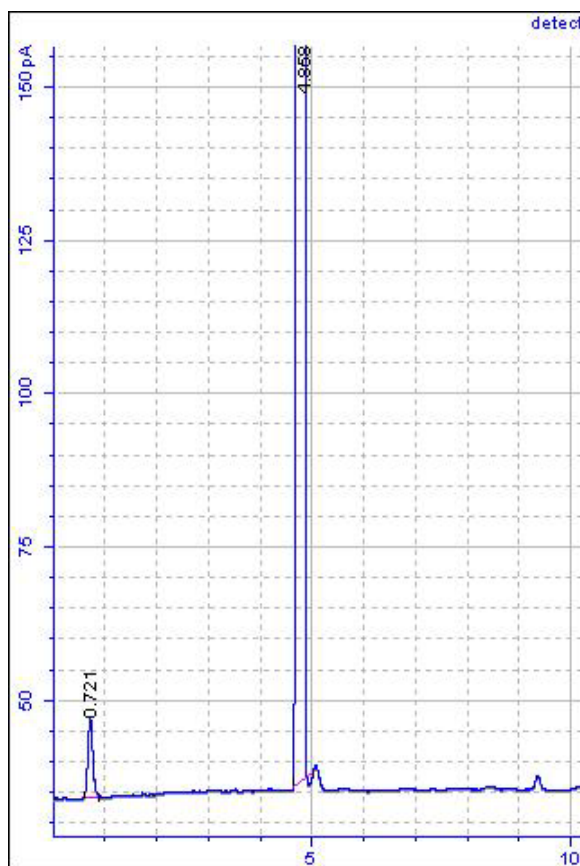


Figure 1. Gas chromatography analysis for injected liquid hydrous ethanol fuel.

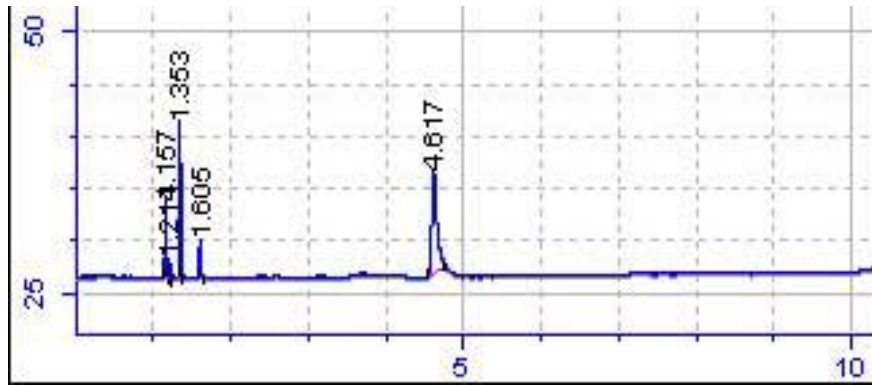


Figure 2. Exhaust aldehydes obtained by gas chromatography at 2000 rev/min engine speed.

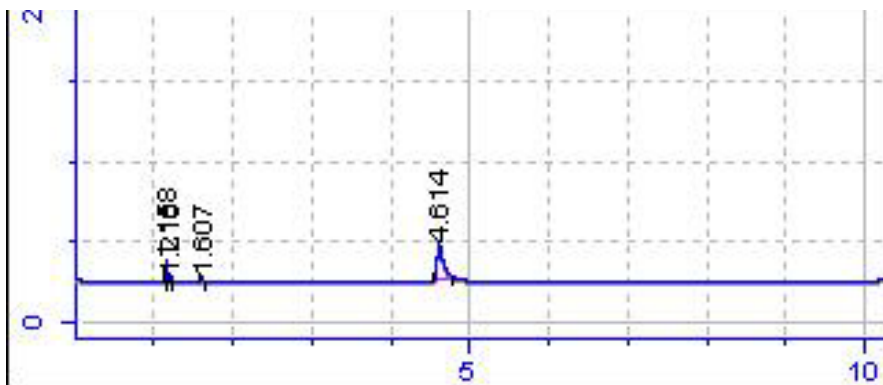


Figure 3. Exhaust aldehydes obtained by gas chromatography at 3000 rev/min engine speed.

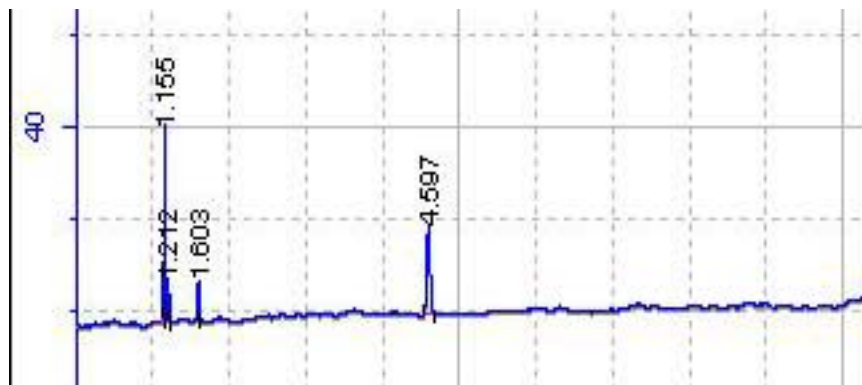


Figure 4. Exhaust aldehydes obtained by gas chromatography at 4000 rev/min engine speed.

Table 2 – Data from chromatogram of Fig. 11 for ethanol fuel analysis.

COMPONENT	CHEMICAL FORMULA	RETENTION TIME	PERCENTAGE AREA	ESTIMATED CONCENTRATION
Ethanol	C ₂ H ₅ OH	4.858 min	87.84775 %	93.2%

Table 3 – Chromatograph aldehyde analysis data at 2000 rev/min.

COMPONENT	CHEMICAL FORMULA	RETENTION TIME	PERCENTAGE AREA	ESTIMATED CONCENTRATION
Methane	CH ₄	1.157 min	0.04667 %	233 ppm
Formaldehyde	CH ₂ O	1.214 min	0.01126 %	56 ppm
Acetaldehyde	C ₂ H ₄ O	1.605 min	0.03631 %	181 ppm
Ethanol	C ₂ H ₅ OH	4.617 min	0.40119 %	1999 ppm

Table 4 – Chromatograph aldehyde analysis data at 3000 rev/min.

COMPONENT	CHEMICAL FORMULA	RETENTION TIME	PERCENTAGE AREA	ESTIMATED CONCENTRATION
Methane	CH ₄	1.158 min	0.01590 %	427 ppm
Formaldehyde	CH ₂ O	1.216 min	0.00375 %	101 ppm
Acetaldehyde	C ₂ H ₄ O	1.607 min	0.00790 %	212 ppm
Ethanol	C ₂ H ₅ OH	4.614 min	0.20654 %	5546 ppm

Table 5 – Chromatograph aldehyde analysis data at 4000 rev/min.

COMPONENT	CHEMICAL FORMULA	RETENTION TIME	PERCENTAGE AREA	ESTIMATED CONCENTRATION
Methane	CH ₄	1.155 min	0.27146 %	320 ppm
Formaldehyde	CH ₂ O	1.212 min	0.06200 %	73 ppm
Acetaldehyde	C ₂ H ₄ O	1.603 min	0.08831 %	104 ppm
Ethanol	C ₂ H ₅ OH	4.597 min	0.55949 %	660 ppm

Another aspect of the method presented that requires further optimization is the chromatograph settings. Use of helium instead of hydrogen as the carrier gas may help to separate the chromatogram peaks arising at about 1.2 min (Figs. 4 to 6). Also, a smoother oven temperature ramp must be adopted for better peak separation and chromatogram base maintenance after 10 min run (not shown in the figures). Finally, a higher split ratio can improve the shape of the chromatogram peaks. The technique presented may become a generalized standard for production engine laboratory test after the optimizations suggested.

5. CONCLUSIONS

- Unburned ethanol, acetaldehyde and formaldehyde has been identified and quantified by gas chromatography using direct exhaust sampling from a hydrous ethanol fueled engine, tested experimentally on a bench dynamometer in the speed range from 2000 to 4000 rev/min.
- Formaldehyde, acetaldehyde, and unburned ethanol retention times were consistent throughout the engine speed range investigated.
- It was not observed a clear trend for formaldehyde, acetaldehyde and unburned ethanol variation with engine rotational speed, requiring further investigation.
- Formaldehyde and acetaldehyde gas chromatography analysis using direct sampling from engine exhaust proved to be an adequate method to quantify these pollutants, being an alternative option to the conventional DNHP/HPLC method.

6. ACKNOWLEDGEMENTS

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