Comparing Unburned Fuel Emission from a Pre-chamber Engine Operating on Alcohol Fuels using FID and FTIR Analyzers

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Abstract

Typical automotive emission testing systems usually employ Flame Ionization Detection (FID) analyzers to measure unburned fuel species in the exhaust, but the technique is not suitable for engines operating on alcohol fuels. The FID method is not sensitive to measuring unburned alcohol fuels due to the presence of oxygen bonds in the fuel molecule. Other techniques, such as Fourier Transform Infrared (FTIR), can provide accurate unburned fuel measurements with alcohol fuel. However, these techniques are expensive and are less accessible compared to FID analyzers. In this study, the unburned fuel emissions from the engine exhaust were measured simultaneously with FID and FTIR analyzers, with the engine operating on pure alcohols, which are methanol, ethanol, and n-butanol. While most previous work focuses on stoichiometric air-fuel mixtures, a wide range of lean operating conditions between global-λ 1.6 to 2.8 will be tested in this study. Such ultra-lean operation was achievable thanks to the narrow-throat pre-chamber combustion concept with the pre-chamber fueled with methane. The unburned fuel measurements from the two analyzers are compared, and correction factors for each fuel are identified to rectify the FID unburned fuel measurements based on the results provided by the FTIR.

Introduction

Along with the growing concern about climate change due to anthropogenic carbon emissions, many government and regulatory bodies have been increasingly focused on reducing the carbon emissions from the transport sector, which accounts for about 23% of global carbon emissions [1]. Many solutions have been proposed to achieve this aim, such as electrifying the light-duty fleet and adopting low carbon or carbon-neutral fuels instead of conventional fuels derived from crude oil. Alternative fuels, such as methanol, ethanol, and butanol, can be derived from biomass or chemical systems and have desirable properties such as high auto-ignition resistance (octane rating) and comparatively faster burning velocity than conventional gasoline.

The high latent heat of vaporization of these alcohol fuels cools down the air-fuel mixture temperature before compression, allowing higher charge densities into the engine, thus improving the volumetric efficiency and the engine power output. Due to their superior octane performance and shorter combustion durations, the engine compression ratio can be increased, which in turn improves the engine thermal efficiency. Faster laminar burning velocities mean the combustion is concluded much sooner, limiting the exhaust losses.

Nowadays, conventional gasoline already contains a certain fraction of ethanol, depending on the country and location. Typical Euro V gasoline contains as much as 5% ethanol by volume, while gasoline with higher blends of ethanol (E10) is the norm in the United States. US Environmental Protection Agency (EPA) also approved E15 gasoline for conventional light-duty vehicles of the model year 2001 in 2011. Blends of conventional gasoline with alcohols and neat alcohols are being studied for conventional combustion modes such as spark ignition (SI) and compression ignition (CI), as well as novel combustion modes such as the homogeneous charge compression ignition (HCCI) and pre-chamber combustion (PCC), also known as turbulent jet ignition (TJI). The latter combustion mode is gaining traction for its improved combustion stability, ultra-low NOx emissions, and high engine thermal efficiency. Attard and Blaxill [2] have demonstrated a maximum engine thermal efficiency of 42% with pre-chamber applications. A higher brake efficiency reaching 45% was demonstrated by Sens et al. [3] by employing a higher compression ratio, EGR dilution, and Miller valve timing coupled with pre-chamber combustion.

Coupling the spark-ignited pre-chamber combustion systems with alcohols is found frequently in the literature to promote the application of low-carbon fuels in standard gasoline engines. Bureshaid et al. [4] discovered that the momentum of the jets is far stronger when operating an optical TJI engine with ethanol. The authors attribute the gain in kinetic energy of the jets to the faster flame speed of ethanol. Similarly, da Costa et al. [5] also observed faster combustion rates and higher dilution tolerance with ethanol-fueled pre-chamber combustion engine studies. Our previous study [6] also indicates that the engine lean operation limit is further enhanced with methanol and ethanol than with gasoline-type fuels. The faster laminar flame speeds of these fuels are of particular importance in pre-chamber combustion systems owing to improved knock resistance and enhanced flame propagation in the main chamber, particularly with lean air-fuel mixtures.

In understanding the combustion characteristics of alcohols, studying the emission characteristics is not straightforward. The conventional automotive emissions analyzers employ the flame ionization detection (FID) method to measure the unburned fuel concentrations in the exhaust. However, FID is not sensitive to unburned oxygenated fuel, aldehydes, and acetaldehydes, which are significant species in the exhaust for alcohol combustion. Several literature studies discuss the relative lower sensitivity of FID analyzer for unburned species with alcohol combustion both with blends of gasoline with methanol [7–10], ethanol [11–14], and n-butanol [15,16] as well as neat alcohol operation [17,18].

Accordingly, researchers typically employed alternative measurement methods, such as the Fourier Transform Infrared
Spectroscopy (FTIR), gas chromatography (GC), and 2,4-dinitrophenylhydrazine (DNPH) cartridge/impinger sampling systems to measure the unburned fuel species. The total unburned hydrocarbons measured from the aforementioned analysis methods are compared against the FID emission concentration to determine the FID correction factor for alcohol fuel combustion. Moreover, the sensitivity of the FID also depends on other factors such as the oven temperature, sample line length, and degradation of catalyst used in the FID analyzer [19].

In this study, the FID sensitivity of the unburned alcohol fuel components is determined by examining the emission levels detected by the FID and FTIR analyzers under lean conditions. The two analyzers are installed in the engine exhaust line, and the emissions are recorded simultaneously at different engine operating conditions. Three alcohols, methanol, ethanol, and n-butanol, were employed for this study.

Pre-chamber Design

The dimensions of the pre-chamber body used in this study are shown in Figure 1. The number of nozzle holes is 12, separated into two layers since the nozzle tip is narrow. The pre-chamber volume is approximately 5.07 cc, corresponding to around 2.5 % of the engine clearance volume with an 11.5 geometric compression ratio. The nozzle hole diameter is chosen so that the total nozzle opening area normalized by the pre-chamber volume is around 0.036 cm²/cm³. These design parameters are chosen according to the pre-chamber normalized volume (PC volume/engine clearance volume) and the total nozzle area over the pre-chamber volume parameters recommended by Gussak et al. [20,21] to achieve minimum ignition delay, optimized combustion stability, and lower emission formation.

![Figure 1. Dimensions of the pre-chamber](image)

Detailed geometrical parameters of the pre-chamber assembly are provided in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-chamber Volume</td>
<td>5.07</td>
<td>[cc]</td>
</tr>
<tr>
<td>Pre-chamber Vol./Clearance Vol.</td>
<td>2.5</td>
<td>[%]</td>
</tr>
<tr>
<td>Number of Nozzles</td>
<td>12</td>
<td>[-]</td>
</tr>
<tr>
<td>Nozzle Diameter</td>
<td>1.40</td>
<td>[mm]</td>
</tr>
<tr>
<td>Nozzle Area/Pre-chamber Volume</td>
<td>0.036</td>
<td>[cm²]</td>
</tr>
<tr>
<td>Nozzle Included Angle</td>
<td>134</td>
<td>[deg]</td>
</tr>
<tr>
<td>Throat Diameter</td>
<td>3.30</td>
<td>[mm]</td>
</tr>
<tr>
<td>Throat Length</td>
<td>22</td>
<td>[mm]</td>
</tr>
</tbody>
</table>

The pre-chamber body is fitted inside an adaptor part. The top part of the adaptor accommodates an M8 spark plug (NGK ER9EH), an M5 pressure sensor (AVL GH15DK), a thermocouple to measure the pre-chamber wall temperature, and a fuel channel. A fuel supply pipe, fed by the solenoid injector, is connected to the fuel channel. A check valve (The Lee Company 558 Series) was fitted inside the fuel channel to allow fuel to pass through but check the backflow of combustion gases. Atop the pre-chamber adaptor, a spacer is provided so that the whole assembly can be secured inside the cylinder head by a clamp. More information on the pre-chamber assembly design and fabrication can be found in previous publications [22,23]. A cross-sectioned view of the pre-chamber assembly installed in the cylinder head and the components discussed are shown in Figure 2 (a) and (b), respectively.

![Figure 2. Pre-chamber setup: (a) cross-section view of installation in the cylinder head, and (b) component diagram](image)

Experimental Setup

**Engine Specifications**

The research engine was converted from a diesel engine for pre-chamber experiments. The original engine had six cylinders, five of which were deactivated. A modified intake manifold with pockets for port fuel injectors (PFI) was fitted to the engine intake. The engine control software was written in National Instruments (NI)...
LabVIEW, and the hardware used a NI CompactRio embedded controller. Detailed specifications of the experimental engine setup can be found in Table 2.

Table 2 - Experimental engine specifications

<table>
<thead>
<tr>
<th>Engine Model</th>
<th>Valve Mechanism</th>
<th>Number of Valves</th>
<th>Bore</th>
<th>Stroke</th>
<th>Connecting Rod Length</th>
<th>Comp. Ratio</th>
<th>Displacement</th>
<th>Intake Valve Timing</th>
<th>Exhaust Valve Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volvo D13C300</td>
<td>Single Overhead Cam</td>
<td>2-Intake 2-Exhaust</td>
<td>131 [mm]</td>
<td>158 [mm]</td>
<td>255 [mm]</td>
<td>11.5 [-]</td>
<td>2.1 [t]</td>
<td>Open/Close</td>
<td>Open/Close</td>
</tr>
</tbody>
</table>

Figure 3. Schematic diagram of the experimental setup

An ABB dynamometer was used to motor the engine and maintain a constant engine speed. The main chamber was fitted with a water-cooled pressure transducer (Kistler 7061) to record the pressure. A crank encoder recorded the high-resolution data at a 0.2 CAD interval. The testbed system was fitted with thermocouples, piezoresistive pressure sensors, and flowmeters to monitor the intake air, cooling water, and lubricating oil sub-systems of the engine. A schematic diagram of the engine systems is shown in Figure 3.

The main chamber fuel was provided by an automotive fuel supply pump that fed to a common rail, which supplied two PFI injectors. Only the injector closest to the engine was used since the experiments are focused on low load conditions. The pre-chamber gaseous fuel was provided from a K-type gas cylinder. A Coriolis mass flow meter measured the fuel flow rate injected into the air intake, in addition to a gravimetric measurement using a mass balance. These two measurements were in good agreement with one another, and the Coriolis flowmeter reading was used in data analysis owing to its faster response. The gaseous fuel flow rate to the pre-chamber was regulated by a thermal-type mass flow controller.

The HORIBA MEXA-1700 Motor Exhaust Gas Analyzer was used to detect the emissions species in the exhaust. For total unburned hydrocarbons (THC) measurements, a heated flame ionization detector (FID) was employed in the exhaust analyzer package. Note that the sensor of the emission analyzer is dedicated to hydrocarbons and is insensitive to aldehydes and unburned oxygenates, which are present in the exhaust when running the engine on alcohols [24].

For FTIR measurements, an AVL SESAM i60 FTIR analyzer was used. This analyzer can measure up to 23 species at a 1 Hz data-acquisition frequency. As shown in Figure 3, the two sampling points were prepared on the engine exhaust line downstream of the exhaust backpressure valve. The sampling point locations were very close to one another, with around 60 mm separation between the two. The FID oven temperature also plays a role. In the US, the FID temperature is specified at 113 °C for methanol-fueled vehicles, while in Europe, 190 °C temperature, the usual FID setting, was used [19]. The oven temperature was set to 190 °C in the experiments.

Operating Conditions and Methodology

Experimental Conditions

The experiments were performed at a constant engine speed of 1200 rpm at an intake pressure of 1.5 bar. The pre-chamber was fueled with gaseous methane of 99.5% purity by volume, while the main chamber was fueled with methanol, ethanol, and n-butanol in three sets of experiments. The fuel properties [25,26] are listed in Table 3. The amount of fuel energy injected via the pre-chamber over the total fuel energy supplied to the engine is represented by the term pre-chamber fuel ratio (PCFR) and maintained at 13% for all the operating conditions. The PCFR is defined as follows.

\[
PCFR = \frac{m_{f,PC}Q_{LHV,PC}}{m_{f,PC}Q_{LHV,PC} + m_{f,MC}Q_{LHV,MC}}
\]

where \(m_f\) refers to the amount of fuel injected per cycle, and \(Q_{LHV}\) refers to the lower heating value of the fuel, while \(PC\) or \(MC\) subscript indicates whether the fuel is injected into the pre-chamber or via the air intake, respectively. Note that PCFR is an energy ratio and not a mass ratio.

1. Engine
2. Intake manifold
3. Port fuel injectors
4. Pre-chamber
5. Dynamometer
6. Backpressure valve
7. EGR cooler
8. EGR valve
9. Exhaust gas analyzer
10. FTIR analyzer
11. Lab air valve
12. Airflow meter
13. Air heater
14. Gas admission valve
15. Mass flow controller
16. PC solenoid valve
17. Mass balance
18. Fuel pump
19. Mass flow meter
20. Common rail
A PCFR of 13% was chosen based on past studies where the highest lean operation limit is observed at that fuel fraction [23, 27–29]. After attaining steady-state conditions, a 500-cycle data-set was recorded for emissions recording of each operating condition and averaged emissions are presented in this paper.

Table 3. Comparison of fuel properties

<table>
<thead>
<tr>
<th>Unit</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>n-Butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>CH₃OH</td>
<td>C₂H₅OH</td>
<td>C₄H₁₀OH</td>
</tr>
<tr>
<td>Molecular weight [g/mol]</td>
<td>32.04</td>
<td>46.07</td>
<td>74.12</td>
</tr>
<tr>
<td>Density [kg/m³]</td>
<td>792</td>
<td>785</td>
<td>810</td>
</tr>
<tr>
<td>Lower heating value [MJ/kg]</td>
<td>20.0</td>
<td>26.8</td>
<td>33.1</td>
</tr>
<tr>
<td>Latent heat of vaporization [kJ/kg]</td>
<td>1103</td>
<td>919</td>
<td>706</td>
</tr>
<tr>
<td>Boiling temperature [°C]</td>
<td>64.7</td>
<td>78</td>
<td>117</td>
</tr>
<tr>
<td>Research octane number</td>
<td>106</td>
<td>107</td>
<td>96</td>
</tr>
<tr>
<td>Motor octane number</td>
<td>92</td>
<td>89</td>
<td>78</td>
</tr>
</tbody>
</table>

At 25 °C temperature and 1 atm pressure

The lean limit is defined at the global-λ, where the coefficient of variation of IMEPₕ exceeds 3%. The lowest global-λ condition adopted for this study was 1.6 since the scope of this study is methane and non-methane unburned fuel species are mainly compared to typical PFI injection timings.

On the other hand, the methanol case shows frequent pre-ignition at global-λ 1.6; therefore, this case is also removed from the methanol data-set. The pre-ignition is considered due to an overheating spark plug, judging by the pressure rise occurring in the pre-chamber before the main chamber heat release begins. An engine operating cycle is deemed pre-igniting when the start of pressure rise in the pre-chamber occurs before the spark timing, as shown in Figure 4. The figure presents a 40-cycle sample of the data-set at global-λ1.6, and the color map refers to the cycle number.

Figure 4. Pressure traces for methanol combustion at global-λ 1.6

The experimental operating conditions are summarized in Table 4.

Table 4 - Experimental Operating Conditions

<table>
<thead>
<tr>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine Speed RPM</td>
<td>1200</td>
</tr>
<tr>
<td>Coolant Temp. °C</td>
<td>83 ± 5</td>
</tr>
<tr>
<td>Lub. Oil Temp. °C</td>
<td>85 ± 5</td>
</tr>
<tr>
<td>Intake Temp. °C</td>
<td>30 ± 1</td>
</tr>
<tr>
<td>Intake Press. bar</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>PC Fuel SOI CAD aTDC</td>
<td>-360</td>
</tr>
<tr>
<td>MC Fuel SOI CAD aTDC</td>
<td>-150</td>
</tr>
<tr>
<td>Spark Timing CAD aTDC</td>
<td>-15</td>
</tr>
<tr>
<td>PC Fuel</td>
<td>Methane (&gt; 99.85% by wt.) Ethanol (&gt; 99.80% by wt.) n-Butanol (&gt; 99.40% by wt.)</td>
</tr>
<tr>
<td>PC FR</td>
<td>1.3 ± 0.5%</td>
</tr>
<tr>
<td>Global-λ</td>
<td>1.8 to lean limit for methanol 1.6 to lean limit for n-butanol 2.0 to lean limit for n-butanol</td>
</tr>
<tr>
<td>Lean Limit</td>
<td>CoV of IMEPₕ &gt; 3%</td>
</tr>
<tr>
<td>Knock Limit</td>
<td>MAPO &lt; 3 bar</td>
</tr>
</tbody>
</table>

Note that the fuel is injected into the air intake during the closed-valve period of the intake valves. As deduced in previous studies [6, 30], this injection method allows better evaporation of fuel since lower unburned fuel in the exhaust was detected compared to typical PFI injection timings.

The engine combustion efficiency is calculated from the emissions using Equation (2).

$$\eta_c = 1 - \frac{\sum m_i Q_{LHV,i}}{m_{PC} Q_{LHV,PC} + m_{MC} Q_{LHV,MC}}$$

(2)

where \(m_i\) refers to the mass concentration and \(Q_{LHV,i}\) refers to the lower heating value of a particular unburned fuel species \(i\) in exhaust listed in Table 5. The subscripts a, b, and c in non-methane unburned fuel species in Table 5 refer to the equivalent carbon, hydrogen, and oxygen numbers for the fuel injected into the main chamber.

The concentration of unburned components and their lower heating values are used to identify the combustion losses [25]. Four species are used in the combustion efficiency calculation, as listed in Table 5. The unburned fuel part is divided into methane and non-methane unburned fuels. The lower heating value of the latter is taken to be the same as that of the main chamber fuel.

Table 5. Unburned components and their lower heating values

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>LHV [MJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>50.0</td>
</tr>
<tr>
<td>Non-methane Unburned Fuel</td>
<td>C₄H₁₀O₂</td>
<td>LHV of MC fuel</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>CO</td>
<td>10.1</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H₂</td>
<td>120.0</td>
</tr>
</tbody>
</table>

The main goal of the study is to identify a correction factor for FID measurements to account for the unburned oxygenates in the exhaust in addition to methane and non-methane hydrocarbons. In this way, the combustion efficiency can be calculated more accurately while still using the FID analyzer. Measurements of methane in the exhaust are almost identical between the FID and FTIR analyzers; therefore, the non-methane unburned fuel species are mainly compared in this study. The concentration of NMHC is calculated
by subtracting the CH₄ concentration from the THC emissions, with a correction for the relative sensitivity of the THC analyzer to CH₄.

\[ \text{NMHC ppmC} = \text{THC ppmC} - (\text{CH}_4 \text{ ppmC} \times \text{CH}_4 \text{ response factor in THC}) \]  

(3)

In the case of FTIR, the non-methane organic gases (NMOG) are used to compare against FID-NMHC. By definition, NMOG is the sum of non-methane hydrocarbons and some oxygenated hydrocarbon species (OHC), such as unburned alcohols and carbonyls [31]. With the additional species measured with the FTIR, the NMOG emissions can be calculated as expressed in Equation (4).

\[ \text{NMOG ppmC} = \text{NMHC ppmC} + \text{CH}_3\text{OH ppmC} + \text{HCHO ppmC} + \text{CH}_2\text{CHO ppmC} \]  

(4)

The NMHC and NMOG emissions are virtually identical in magnitude when the fuel does not contain alcohol but deviates significantly for alcohol combustion. Comparing FTIR-NMHC against the FID-NMHC would discount the unburned oxygenates, which goes against the aim of this investigation.

Instead of ppmC emissions, the emissions index can also indicate the mass of unburned species emitted per unit mass of fuel. The unit is usually expressed as g/kg-fuel.

\[ E_{l_i} = \frac{m_{l_i}}{m_f} \times 1000 \]  

(5)

where \( i \) represents the exhaust species of interest, \( m_{l_i} \) refers to the mass flow rate of the said species in the exhaust, and \( m_f \) is the total fuel flow rate supplied to the engine.

The mass flow rate of individual species is calculated by Equation (6) [19].

\[ m_{l_i} = \dot{V}_{\text{mix}} Q_i C_i \times 10^{-6} \]  

(6)

where \( \dot{V}_{\text{mix}} \) is the volume flow rate of exhaust gases at STP, \( Q_i \) is the density of species \( i \) at STP, and \( C_i \) is the concentration of pollutant \( i \) expressed in ppmC.

Results and Discussion

The results and discussion section comprises four sub-sections: (1) engine performance and combustion characteristics, (2) comparison of unburned fuel species between the FTIR and FID analyzers, (3) the unburned species analysis, and (4) FID correction factor determination.

Engine performance and combustion characteristics

The engine performance parameters and the combustion characteristics are shown in Figure 5. For the global-\( \lambda \) range adopted in this study, the IMEP\textsubscript{g} ranges between 6.3 and 11.5 bar for the leanest and lowest global-\( \lambda \), respectively.

Methanol consistently shows a slightly higher gross indicated efficiency than ethanol and n-butanol across the global-\( \lambda \) range in this study. Apart from global-\( \lambda \) 2.0, n-butanol shows higher gross indicated efficiency than ethanol. Due to its lower auto-ignition resistance, n-butanol combustion at global-\( \lambda \) 2.0 shows significant end-gas auto-ignition or knock that is known to exacerbate heat transfer losses. However, since the spark timing is fixed at -15 CAD aTDC, the combustion phasing is not optimized, as shown in the middle plot of Figure 5 (b). Further improving the combustion phasing may bridge the gap in gross indicated efficiency between the three alcohol fuels. The combustion stability parameter (CoV of IMEP\textsubscript{g}) is similar between methanol and ethanol. N-butanol shows slightly higher cycle-to-cycle variations. In general, the CoV of IMEP\textsubscript{g} is lower than 3\%, and the three alcohol fuels have similar lean limits.

The pre-chamber pressure buildup, denoted by (\( \Delta P_{\text{pre:MC}} \)), is almost identical for all three fuels for all the global-\( \lambda \) conditions. In general, the combustion durations (CA10-90) are relatively short, a characteristic of active pre-chamber combustion. At each global-\( \lambda \), the combustion duration is shorter with methanol compared to ethanol, perhaps due to the faster laminar burning velocity of methanol. The shorter combustion duration increases the gross-indicated efficiency of methanol combustion so that it is higher than the other fuels. On the other hand, n-butanol shows a faster combustion duration than ethanol, leading to its gross indicated efficiency being higher than ethanol for most global-\( \lambda \) conditions.
Figure 5. Engine performance and combustion characteristics: (a) gross indicated mean effective pressure, gross indicated efficiency, and combustion variability, and (b) pre-chamber pressure buildup, combustion phasing (CA50), and combustion duration (CA10-90)

Comparison of unburned fuel species between the FTIR and FID analyzers

The emission indices of methane and non-methane unburned fuel emissions and the combustion efficiency calculations are compared between the FTIR and FID analyzers in Figure 6. Figure 6 (a) shows that the methane emissions measurements are almost identical between the two analyzers. Similarly, the unburned carbon monoxide emission is virtually identical between the FID and FTIR analyzers. Since methane is very sensitive to FID measurements, the unburned non-methane emissions are mainly used to correct the NMHC measurements from the FID analyzer. The unburned non-methane emissions refer to NMHC measurement for the FID analyzer and NMOG emissions for the FTIR results.

Figure 6 (b) shows that the non-methane unburned fuel emission index values increase with global-λ for all three fuels. Methanol shows the lowest incomplete combustion, followed by ethanol and n-butanol. As a result, methanol operation has the highest combustion efficiency while n-butanol has the lowest. Due to the lower sensitivity of unburned oxygenates in the exhaust by the FID analyzer, using only the FID measurements would result in a 1 to 2% overestimation in combustion efficiency, as presented in Figure 6 (c), with relatively the highest overestimation for n-butanol.

Figure 6. Emission index of unburned fuel emissions: (a) raw methane emissions, (b) raw non-methane emissions, and (c) combustion efficiency
**Unburned species analysis**

The engine-out ppm emissions from the FTIR for various species are presented in Figure 7. Some species, such as iso-pentane, hydrogen cyanide, and carbonyl sulfide emissions, are non-existent and are not shown here. The hydrocarbon (HC) emissions, shown in Figure 7 (a) and (b), are dependent on the carbon number of the fuels since the emission levels with methanol are practically zero. The emissions are consistently higher for n-butanol, followed by ethanol, except for ethane (C_2H_6) emissions, where n-butanol shows zero-emission values.

As expected, ethanol and n-butanol do not show methanol emissions, as presented in Figure 7 (c). Similarly, unburned ethanol emissions are highest for ethanol combustion, followed by n-butanol with zero ethanol emissions from methanol combustion.

The aromatic hydrocarbon emissions (AHC) are highest for methanol, while other fuels do not show significant values. The higher AHC emissions with methanol are potentially due to the high latent heat of the fuel compared to the other fuels, effectively cooling down the in-cylinder charge. In addition, for a particular global-λ, a significantly higher mass of fuel was injected in the case of methanol, probably leading to lower mixture homogeneity.

![Figure 7. Unburned species analysis: (a) acetylene, ethylene, and ethane, (b) propene, 1,3 butadiene, and n-pentane, (c) methanol, ethanol, and aromatic hydrocarbons, and (d) formaldehyde, acetaldehyde, and carbon monoxide](image)

**FID correction factor determination**

The calculated overall FID correction factors for unburned fuel, including both NMHC and OHC compounds, are shown in Figure 8. The correction factors are calculated using the following expression.

\[
FID \text{ Correction factor} = \frac{FID - NMHC \text{ ppmC}}{FTIR - NMOC \text{ ppmC}} \tag{7}
\]

where \(FID - NMHC \text{ ppmC}\) refers to the non-methane hydrocarbons measured from FID, and \(FTIR - NMOC \text{ ppmC}\) refers to the non-methane organic gases measured from FTIR in ppm.

Instead of ppmC emissions, the emission index can also be used to derive the FID correction factor.

\[
FID \text{ Correction factor} = \frac{FID - EI_{NMHC}}{FTIR - EI_{NMOC}} \tag{8}
\]

where \(FID - EI_{NMHC}\) refers to the emission index of non-methane hydrocarbons calculated from FID measurements, and \(FTIR - EI_{NMOC}\) refers to the emission index of non-methane organic gases calculated from FTIR measurements.

The correction factors derived from Equation (7) and (8) are presented in Table 6. For each of the fuels tested, the FID corrections factor from ppmC emissions and the emission index are very similar with some minor offset. Linear curve fitting was applied to the calculated correction factors. The values of the intercepts and slopes are given in Table 7.

![Table 6. FID correction factors calculated from this study](image)
For unburned hydrocarbons other than methane, the FID response factor is unity, meaning that these HC species are perfectly sensitive to FID measurement. The default response factors for oxygenates provided in US EPA regulation [32] are given in Table 7.

Table 7. Default values of FID response factors for unburned oxygenates from US EPA regulation [32]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Response Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>CH$_3$CHO</td>
<td>0.50</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C$_2$H$_5$OH</td>
<td>0.75</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>HCHO</td>
<td>0.00</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH$_3$OH</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Figure 7 (c) shows that unburned methanol increases gradually with leaner global-λ conditions when the engine is fueled with methanol. On the other hand, the formaldehyde emission from methanol combustion increases as the global-λ reduces but maintains a steady value beyond global-λ 2.0 (Figure 7 (d)). For methanol, since formaldehyde is less sensitive to FID measurement than methanol, the high formaldehyde emissions resulted in a lower correction factor at lower global-λ conditions, giving the overall increasing gradient of the correction factor with global-λ, as shown in Figure 8 (a).

Similarly, the gradient is also positive with ethanol combustion. Compared to methanol combustion, unburned ethanol emissions are more sensitive to global-λ and increase significantly as the mixture becomes leaner. Before global-λ 2.0, acetaldehyde emissions were more significant than formaldehyde emissions. The two emissions become similar in magnitude beyond global-λ 2.0. Acetaldehyde emissions are less sensitive to FID than ethanol, giving a positive slope of a linear trend with this fuel. In contrast to methanol, ethanol shows noticeable acetylene and ethylene emissions for the relatively rich global-λ, leading to its correction factor being slightly higher than methanol, as depicted in Figure 8 (b).

For n-butanol combustion, acetylene, ethylene, and propene emissions are much more significant than ethanol. As a result, its correction factor is higher than ethanol. As the mixture becomes leaner, these HC emissions decline and become comparable with formaldehyde and acetaldehyde emissions. Hence, the linear fit of the correction factor shows a downward trend, as presented in Figure 8 (c).

Some of the FID correction factors found in the literature are also included in Figure 8 to compare against the values derived from the current study. Due to the lack of available data in lean conditions in the literature (which this study sets out to connect), only the correction factors at stoichiometric conditions are shown. Some available data are only based on a single oxygenate species, such as the correction factor indicated by Sandstroem-Dahl et al. [19], using only the ethanol sensitivity to FID. Even in the literature, the correction factors reported vary widely due to the differences in FID oven temperature, sample line lengths, and degradation of the NMHC catalyst. Therefore, it is always advisable to determine the correction factor of a specific FID analyzer against an alternative unburned oxygenates detection method such as FTIR, gas chromatography, or impinger tests.

**Summary**

Lean and ultra-lean combustion of methanol, ethanol, and n-butanol was successfully achieved in an active pre-chamber combustion engine operation by fueling the pre-chamber with methane. Stable combustion (< 3% CoV of IMEPg) was achieved with all the fuels while maintaining short combustion durations. Note that the engine combustion phasing is not optimized since the spark timing was fixed. For non-optimized combustion phasing, methanol shows the highest gross indicated efficiency, reaching a maximum of 44%. In comparison, ethanol and n-butanol achieve the highest efficiencies of 42% at different global-λ conditions.

FID correction factors were established from simultaneous emission analysis with FID and FTIR analyzers at lean conditions. This work was done to fill a gap in the literature. Using the FTIR measurements, the evolution of unburned hydrocarbon and oxygenates as the global-λ increases are studied. It was also demonstrated that using the FID measurements alone would result in over-estimation of combustion efficiency by as high as 2%. Linear trends for FID correction factors were determined by comparing the FID and FTIR non-methane unburned fuel emissions. In general, when extrapolated back to global-λ = 1 conditions, the calculated correction factors are in good agreement with the values found in the literature.
The current study focuses on the lean conditions, and the same methodology can be applied for relatively richer conditions or stoichiometry. Another interesting concept is to compare the FTIR and FID measurements with EGR dilution applications. Since EGR reduces the bulk gas temperatures during combustion, the exhaust speciation analysis using FTIR measurements can provide the evolution of potentially toxic species such as formaldehyde and acetaldehyde at diluted conditions not covered in the current study.

References


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## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>AHC</td>
<td>Aromatic hydrocarbon</td>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<td>C₂H₂</td>
<td>Acetylene</td>
<td>HCHO</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>Ethylene</td>
<td>IMEPg</td>
<td>Gross indicated mean effective pressure</td>
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<tr>
<td>C₂H₆</td>
<td>Ethane</td>
<td>λ</td>
<td>Excess air ratio</td>
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<tr>
<td>C₃H₆</td>
<td>Propene</td>
<td>MC</td>
<td>Main chamber</td>
</tr>
<tr>
<td>C₄H₆</td>
<td>1,3 Butadiene</td>
<td>nm-C₅H₁₂</td>
<td>Non-methane hydrocarbons</td>
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<tr>
<td>n-C₅H₁₂</td>
<td>n-Pentane</td>
<td>NMHC</td>
<td>Non-methane hydrocarbons</td>
</tr>
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<td>CH₃OH</td>
<td>Methanol</td>
<td>NMOG</td>
<td>Non-methane organic gases</td>
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<td>CH₃CHO</td>
<td>Acetaldehyde</td>
<td>OHC</td>
<td>Oxygenated hydrocarbons</td>
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<td>C₂H₅OH</td>
<td>Ethanol</td>
<td>P</td>
<td>Pressure</td>
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<tr>
<td>CA10</td>
<td>Crank angle at 10% of cumulative heat release</td>
<td>PC</td>
<td>Pre-chamber</td>
</tr>
<tr>
<td>CA90</td>
<td>Crank angle at 90% of cumulative heat release</td>
<td>ppm</td>
<td>Parts per million</td>
</tr>
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<td>CAD aTDC</td>
<td>Crank angle degree after top-dead-center</td>
<td>ppmC</td>
<td>Parts per million on C1 basis</td>
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<tr>
<td>CoV</td>
<td>Coefficient of variation</td>
<td>Q_{LHV}</td>
<td>Lower heating value</td>
</tr>
<tr>
<td>EI</td>
<td>Emission index</td>
<td>SI</td>
<td>Spark ignition</td>
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<tr>
<td>FID</td>
<td>Flame ionization detection</td>
<td>T</td>
<td>Temperature</td>
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<tr>
<td></td>
<td></td>
<td>THC</td>
<td>Total hydrocarbons</td>
</tr>
<tr>
<td></td>
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